PB-222 938

ENVIRONMENTAL APPLICATIONS OF ADVANCED INSTRUMENTAL ANALYSES: ASSISTANCE PROJECTS, FY 69-71

Lawrence H. Keith, et al

Environmental Protection Agency
Athens, Georgia

May 1973

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EPA-R2-73-155
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PB 222 938

Environmental Protection Technology Series

W73.13662

Environmental Applications of Advanced Instrumental Analyses: Assistance Projects, FY 69-71

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SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No. 2. W73-13662

ENVIRONMENTAL APPLICATIONS OF ADVANCED INSTRUMENTAL ANALYSES: ASSISTANCE PROJECTS, FY 69-71,

5. Report Date

8. Performing Organization Report No.

Lawrence H. Keith and Shirley H. Hercules

EPA Project 16020 GHZ

Environmental Protection Agency, Athens, Georgia, National Water Contaminants Characterization Research Program, Southeast Environmental Research Laboratory.

13. Type of Report and Period Covered

Environmental Protection Agency

Environmental Protection Agency report number EPA-R2-73-155, May, 1973. 82p, 28 fig, 23 tab, 14 ref.

A multitude of analyses using gas chromatography-mass spectrometry (GC-MS), nuclear magnetic resonance (NMR), infrared, and fluorescence spectroscopy to identify and measure organic pollutants in water are discussed under eleven project categories. In most cases these analyses have helped to solve, or at least understand more clearly, the related pollution incident and in some cases provided for enforcement of regulatory legislation. Projects included identification of pesticides and PCB's from natural waters, organics from industrial wastewaters and landfill runoffs, organics from paper mill wastewaters and foam, and analyses of oils from oil spills and suspect sources. (EPA)

*Water pollution, *Chemical wastes, *Chemical analyses, *Mass spectrometry, *Oil spills, *Pesticides, *Fishkill, *Polychlorinated biphenyls, *Organoleptic properties, *Nuclear magnetic resonance, *Fluorometry, Taste, Odor, Oil pollution, Paper mill pollution, Phthalates, Fatty acids, Resin acids

05A

Copy available from GPO Sup Doc as 73-135 23/2 $ .25; microfiche from NTIS as PB 222 138.

19. Security Class (Report)

21. No. of Pages

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EPA-R2-73-155
May, 1973

ENVIRONMENTAL APPLICATIONS OF ADVANCED INSTRUMENTAL ANALYSES: ASSISTANCE PROJECTS, FY 69-71

by

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ABSTRACT

A multitude of analyses involving the identification and measurements of organic pollutants in water are discussed under eleven project categories. In most cases these analyses have helped to solve, or at least understand more clearly, the related pollution incident and in some cases provided evidence for enforcement of regulatory legislation.

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ACKNOWLEDGMENTS

The following NWCCRP staff were the principal investigators of the projects listed in Section IV:

Project	
1.	L. H. Keith and A. W. Garrison
2.	A. W. Garrison and A. D. Thruston, Jr.
3.	A. W. Garrison
4.	A. W. Garrison
5.	R. G. Webb
6.	A. W. Garrison and L. H. Keith
7.	L. H. Keith
8.	C. G. Gustafson
9.	L. H. Keith
10.	L. H. Keith
11.	A. D. Thruston, Jr.

The assistance of A. L. Alford, T. L. Floyd, F. R. Allen, A. C. McCall, and M. M. Walker in preparing the samples for analysis, providing spectral data, interpretation of spectra, and confirmation with standards is gratefully acknowledged.

SECTION I

CONCLUSIONS

The identification and quantification of specific chemical compounds responsible for a wide variety of pollution incidents have helped to solve, or at least to understand more clearly, the problems associated with the incidents. In some cases evidence was provided for enforcement of regulatory legislation. The projects have demonstrated the applicability of newly developed laboratory techniques to environmental pollution problems.

Because of the complexity and small size of the samples available, gas chromatography-mass spectrometry has been the most valuable technique for analysis. Nuclear magnetic resonance and infrared spectroscopy were helpful when a single compound was isolated in sufficient quantity.

SECTION II

RECOMMENDATIONS

Analyses of the type described will be necessary and should be used for establishing and enforcing water quality effluent standards for the industrial permit program. The data provided will also be needed to update these standards with respect to specific organic compounds discharged into receiving waters. Many more laboratories, including those at the state level, should be equipped to conduct the type of analyses described herein.

Newly developed techniques should be investigated for their applicability to pollution analysis.

An annual report of unpublished contaminants characterization work is recommended.

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SECTION III

INTRODUCTION

The National Water Contaminants Characterization Research Program (NWCCRP) develops methods for the identification and quantification of chemical pollutants and identifies specific compounds associated with various sources of pollution. Information thus obtained may be used in the development of regulatory legislation. In assessing the applicability of new techniques to environmental samples and developing information that the NWCCRP has a unique capability for providing, a number of samples are analyzed that are directly related to a wide range of environmental problems.

Results of the aforementioned analyses are reported in individual memoranda to the person requesting the analysis and therefore receive limited distribution. To acquaint other researchers and administrators with the type of information that can be provided and to help analytical chemists recognize the broad applicability of the techniques used, a series of annual reports is planned. Brief summaries will be presented of the problems under study by the NWCCRP. This first report, summarizing the problems studied during the fiscal years 1968 through 1971, deals mostly with the application of gas chromatography-mass spectrometry since the NWCCRP was the only group in the Federal Water Quality Administration with a GC-MS capability during this period. Future reports will discuss applications for a wider variety of techniques.

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SECTION IV

PROJECTS

1. *Tennessee River Contaminant (bis[2-ethylhexyl] phthalate)*

When the Ohio River is at flood stage, the Tennessee River dam above Calvert City, Kentucky, is closed, releasing little or no flow down the Tennessee River. During the spring of 1968 the dam was closed and the industries on the lower Tennessee River complained about the pooling of industrial wastes under the stagnant river condition.

Samples of the contaminated water were taken by personnel at the Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio. Analysis by flame ionization gas chromatography revealed the presence of one compound whose concentration far exceeded that of all others. IR and GC of chloroform extracts suggested "the presence of a phthalate very similar to dinonyl phthalate" (1). An extract was submitted to the NWCCRP for molecular structural identification.

Both thin layer and gas chromatography indicated that the extract contained only one major component in about 90% purity. The NMR, infrared, and mass spectra were therefore recorded with no further purification. The infrared spectrum (Figure 1) shows peaks characteristic of a carbonyl, an ester, and an ortho substituted phenyl (2). NMR and mass spectra (Figure 2) confirm the presence of a phthalate and indicate it to be a dioctyl phthalate ester.

Fifteen possible isomeric structures exist for dioctyl phthalate, assuming the diester to be symmetrical. Further analysis of the NMR peaks in conjunction with the electronic integration yielded the structure bis[2-ethylhexyl] phthalate (I).

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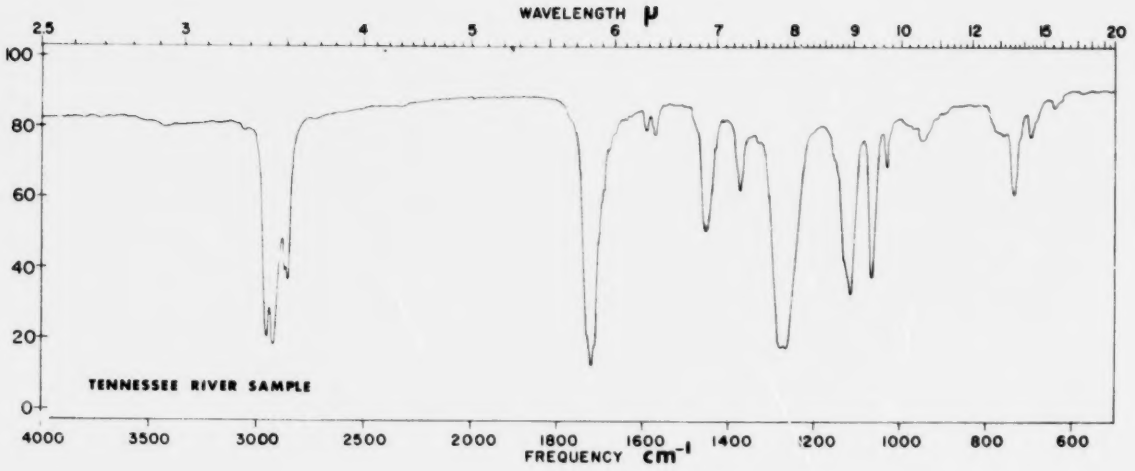


Figure 1. Infrared Spectrum of the Tennessee River Sample

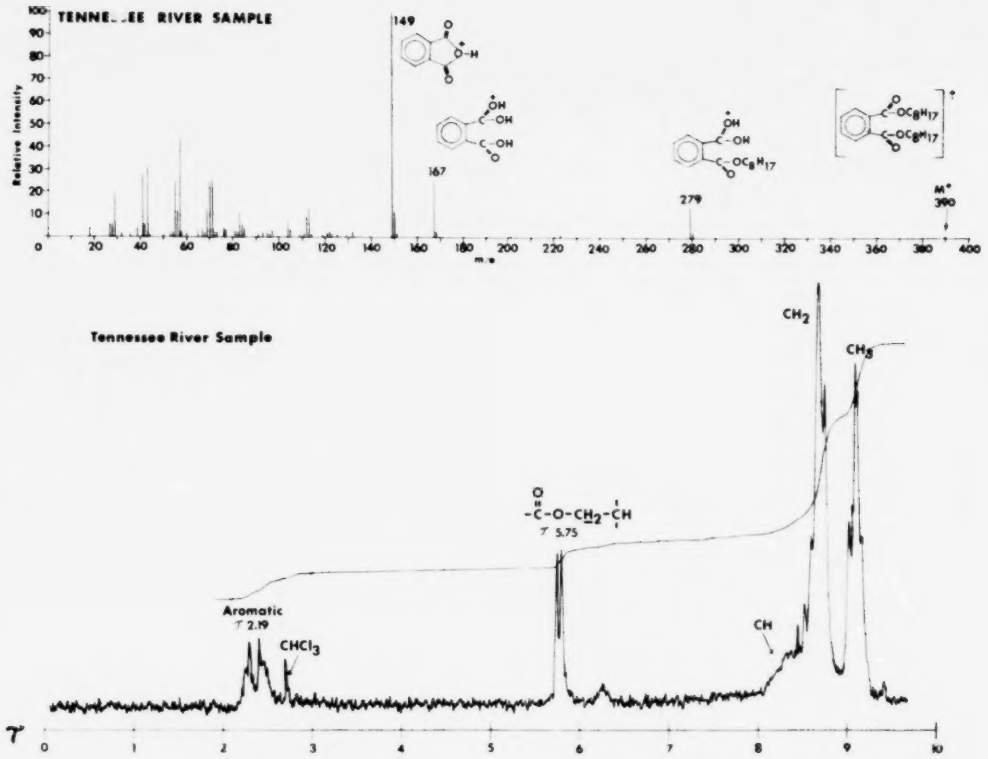
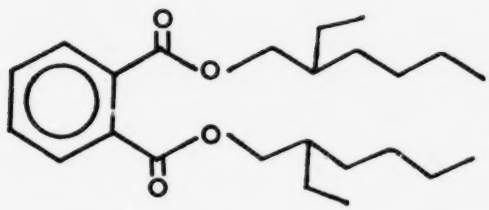


Figure 2. Mass Spectrum (top) and NMR Spectrum (bottom) of Tennessee River Sample



I

Comparison of the NMR, IR, and mass spectra of the sample with those of a standard confirmed the above structure (Figures 3-5).

The results of the structure determination were submitted to the Taft Center.

2. *Fish Kill Contaminant Characterizations (Pesticides)*

Boone Lake

During the summer of 1968 a massive kill of approximately one million fish occurred in the Boone Lake reservoir, Tennessee. After eliminating all of the more common causes of fish kills, the contents of some nearly empty 55-gallon drums found floating on the reservoir were investigated. The metal drums were of the kind commonly used to float docks and boathouses.

The manufacturer listed on one of the drum labels, Buckman Laboratories, Inc., indicated that the drum may have contained a mixture of phenylmercuric acetate and 2,4,6-trichlorophenol, a microorganism control product. Subsequent analysis of the river water and drum residue revealed the presence of the trichlorophenol and diphenyl mercury, a decomposition product of the phenylmercuric acetate. A residue sample analyzed by mass spectrometry using the direct probe inlet was shown to contain phenylmercuric chloride (Figure 6, top). However, recent work in the National Environmental Research Center, Analytical Quality Control Laboratory of Cincinnati, Ohio, indicates that the acetate is readily converted to the chloride. Confirmation of the structure was obtained by comparison of the mass

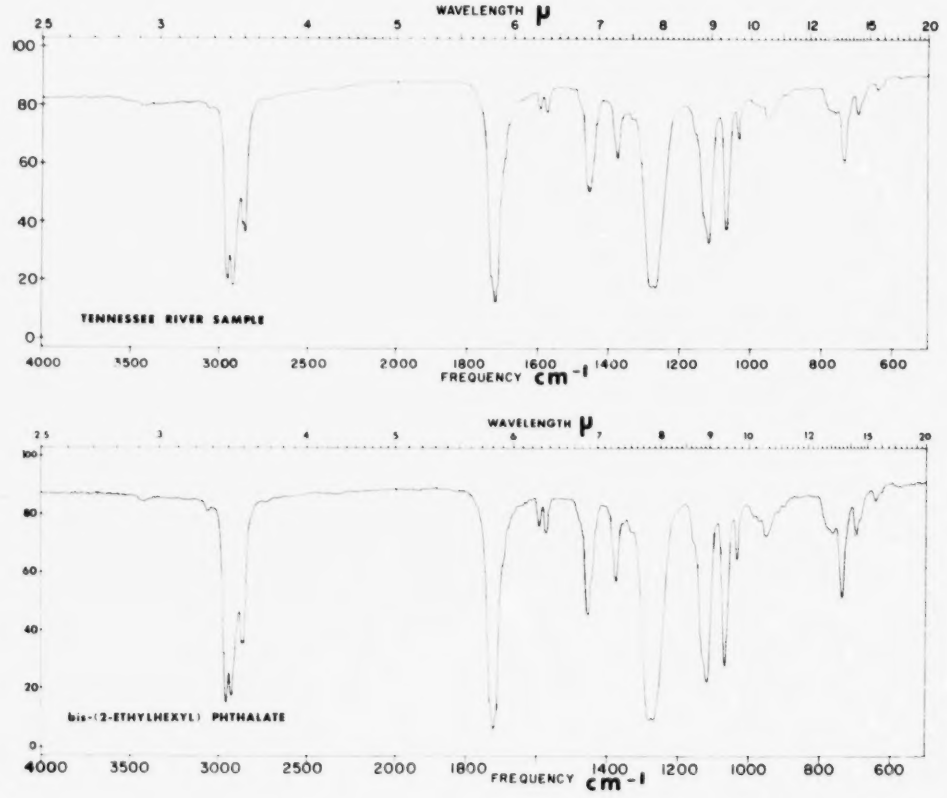


Figure 3. Comparison of the Infrared Spectrum of the Tennessee River Sample with that of bis (2-ethylhexyl)phthalate

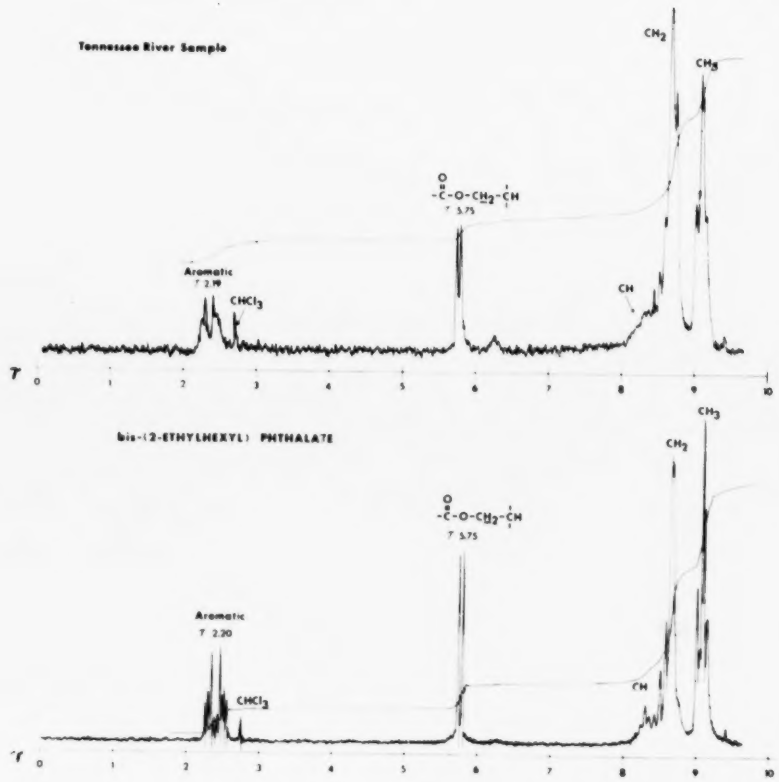


Figure 4. Comparison of the NMR Spectrum of the Tennessee River Sample with that of bis(2-ethylhexyl)phthalate

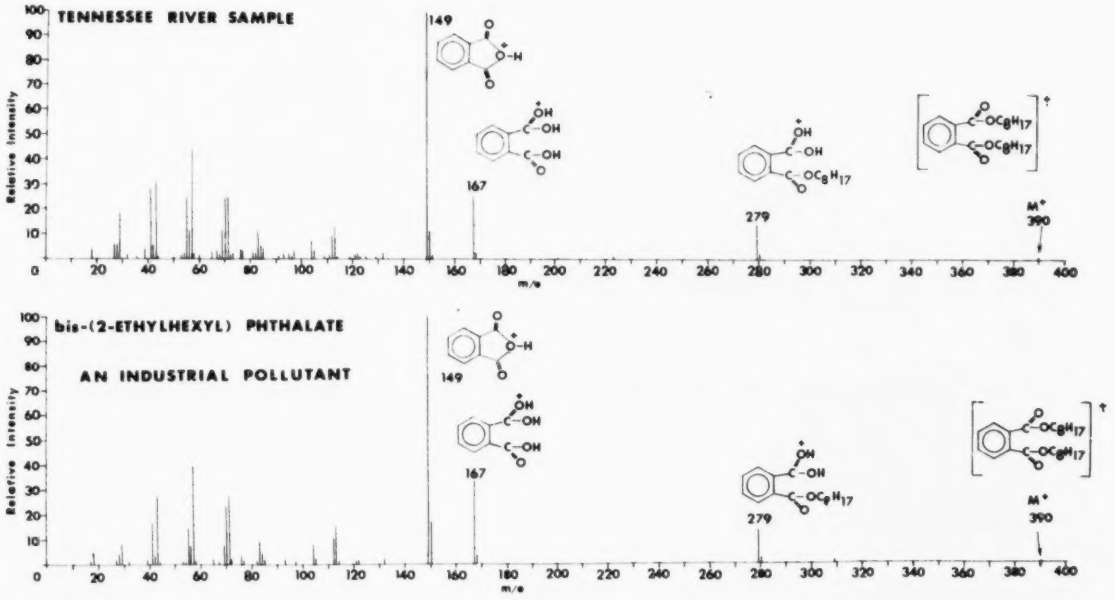


Figure 5. Comparison of the Mass Spectrum of the Tennessee River Sample with that of bis(2-ethylhexyl)phthalate

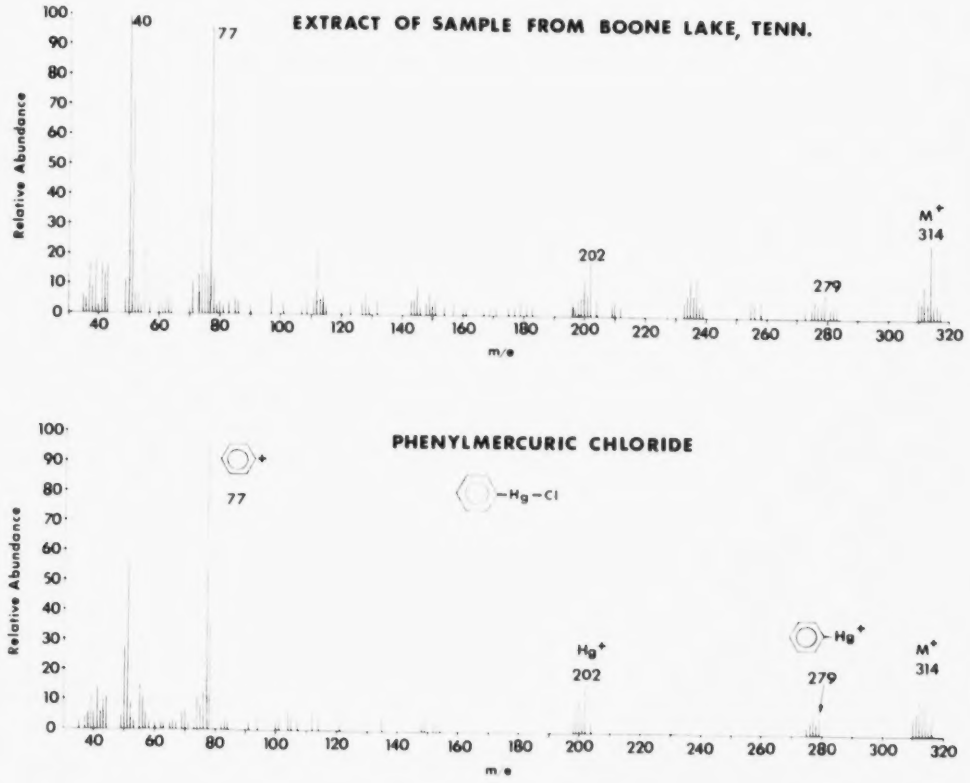


Figure 6. Comparison of the Mass Spectrum of Boone Lake Extract with that of Phenylmercuric Chloride

spectrum with that of a standard (Figure 6, bottom).

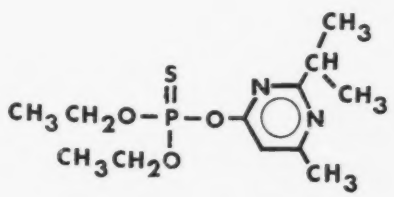
Bioassay conducted by TVA personnel confirmed the toxicity of the phenylmercury compound to fish. Analysis of water samples indicated the presence of diphenylmercury at greater than acutely toxic levels, establishing it as the primary cause of the fish kill.

Beginning October 7, 1968, all drums containing and suspected of containing toxic materials were to be removed from the area of the kill by personnel of the Division of Reservoir Properties. The year 1972 was set by the Tennessee Valley Authority as a deadline for the complete removal from the reservoir of all drums used as flotation devices. A subsequent fish kill in 1969 prompted the suggestion that attempts be made to remove the drums before the suggested deadline.

Tombigbee River, Alabama

In 1968, a fish kill involving about 30 thousand fish occurred on the Tombigbee River in Alabama. Geigy Chemical Corporation, a manufacturer of pesticides among other products, was a suspected source of the contamination that killed the fish.

Gas chromatography indicated the presence of the organophosphorus pesticide, diazinon (II), in the water samples taken from the area of the fish kill, but more substantial evidence was required for legal prosecution.



II

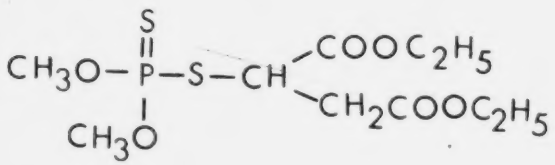
Accordingly, the sample was chromatographed by TLC and the adsorbent containing the spot with an R_f corresponding to that of diazinon was scraped from the plate.

A similar area of adsorbant was scraped from a blank plate. The residues were introduced into the MS by direct probe; subtraction of the peaks present in the spectrum of the blank from the peaks in the river sample spectrum left a fragmentation pattern (Figure 7, top) identical to that of a diazinon standard (Figure 7, bottom) in the region above m/e 100.

A federal court awarded the state damages in the amount of the value of the fish killed.

Black Warrior River and Locust Fork Branch Fish Kills

Fish kills in the Black Warrior River occurred at the Locust Fork Branch, near Birmingport, Alabama in October, 1969, and again near Demopolis, Alabama in September, 1970. The 1969 kill involved 750 thousand fish and the 1970 incident killed 8 thousand fish. Both kills were suspected to have been caused by the spraying of malathion (III) in conjunction with a U. S. Corps of Engineers mosquito control program in this area.



III

The presence of malathion was confirmed by GC-MS in extracts of both the Locust Fork Branch (Figure 8-A) and the Black Warrior River area near Demopolis (Figure 8-B). The molecular ion (m/e 330) was not observed in spectra of either of the samples or of the standard when it was introduced from the gas chromatographic column (Figure 8-C). Instead, the fragment (m/e 173) resulting from cleavage of $(CH_3O)_2PS_2^{\bullet}$ was the largest significant ion. A small parent ion was found in a sample introduced by the direct probe (Figure 8-D). The fragmentation pattern of 8-D is

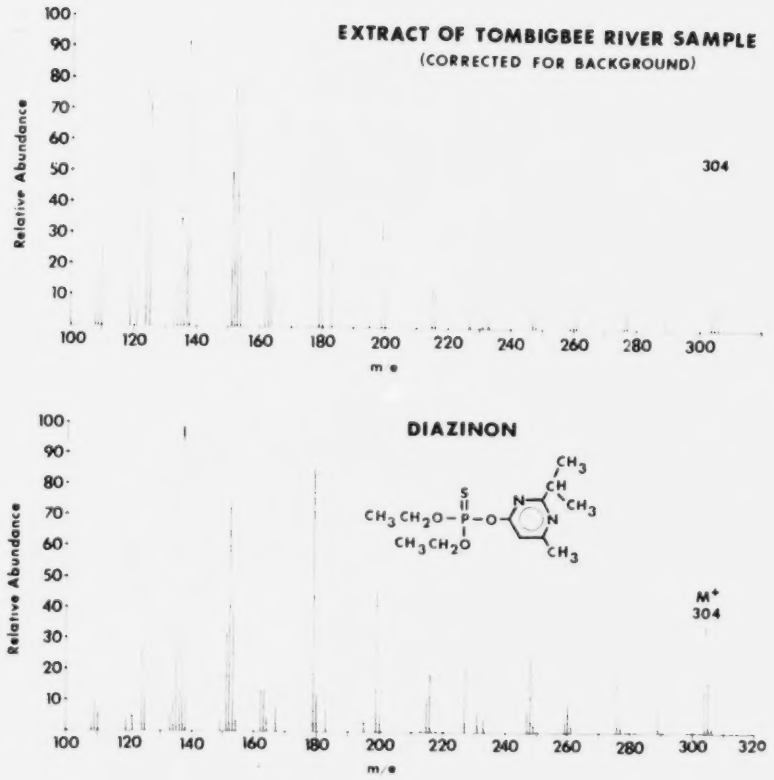


Figure 7. Comparison of the Mass Spectrum of Tombigbee River Extract with that of Diazinon

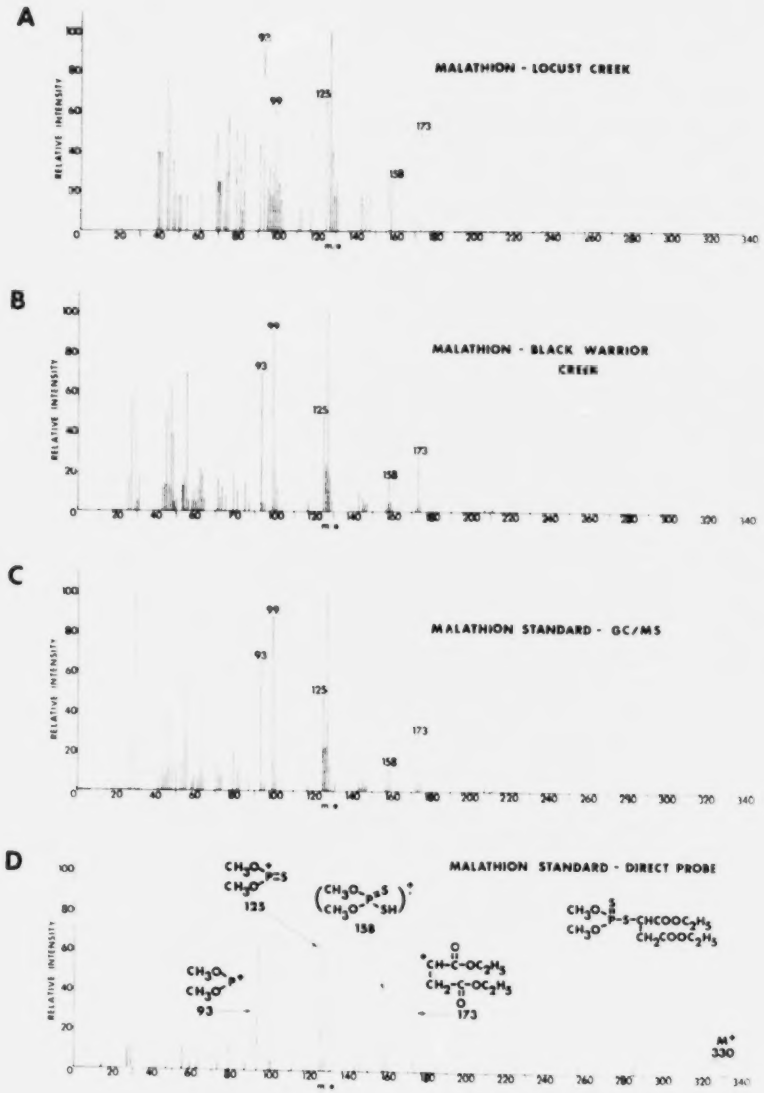


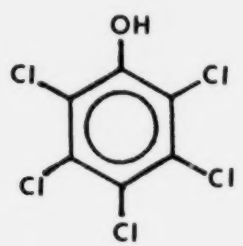
Figure 8. Comparison of the Mass Spectra of the Locust Fork Branch and Black Warrior River Extracts with those of Malathion Obtained by GC-MS and by Direct Probe Insertion

significantly different from 8-C (primarily due to different sample pressures in the ion source), illustrating the necessity of comparing mass spectra of samples with standards under identical conditions. The major fragmentations of malathion are indicated in Figure 8-D.

The results of these analyses were used in a brief prepared by the Alabama Department of Conservation and submitted to the Alabama State Attorney.

Yalobusha River--Mississippi

A kill of an estimated 15 tons of fish occurred in April, 1971, in the Yalobusha River, Grenada, Mississippi. The organic chemical responsible for the kill had been tentatively identified by gas chromatography as pentachlorophenol (IV). Confirmation of the structure was requested for legal action.



IV

The samples and a standard of pentachlorophenol were each methylated with diazomethane and analyzed by GC-MS. Both retention time and mass spectral analysis confirmed the unknown to be pentachlorophenol. The mass spectrum indicated also the presence of tetrachlorophenol isomer in some of the samples.

The results of the structure determination were submitted to the Office of the Attorney General in Mississippi for prosecution.

3. Confirmation of PCB's in Environmental Samples

PCB's (polychlorobiphenyls), manufactured by the chlorination of biphenyl, are distillation fractions containing 20 or more isomers. They have been widely used in a large variety of industrial and consumer products since 1929. Manufactured throughout the world, PCB's are sold in the U. S. solely by Monsanto Company under the trade name Aroclors(R). Because of their resistance to chemical breakdown, PCB's have become ubiquitous polluters of the environment (4).

Only recently has the cumulative chronic toxicity of the chlorinated biphenyls to animal life been observed. It has therefore become important to develop methods for their detection and identification in environmental samples.

Mass spectrometry has been used to confirm the presence of PCB's, tentatively identified by electron capture GC, in water and mud samples. The flame detector chromatograms of the extracts are invariably complicated, but the specificity of the mass spectrometer allows unequivocable identification of submicrogram amounts of PCB's.

Escambia Bay, Florida

In one case an Escambia Bay, Florida, sediment extract cleaned on a Florisil column was analyzed for Aroclor 1254. The GC flame detector pattern is shown in Figure 9. Eleven of the peaks were shown by MS to be due to PCB's. Their retention times and chlorine numbers (number of chlorine atoms per PCB molecule, as determined by MS) correspond with those of an Aroclor 1254 standard, also shown in Figure 9.

Mass spectra showing several chlorine isotope clusters for some of the PCB's from the Escambia Bay sediment are compared with corresponding spectra from an Aroclor 1254 standard in Figure 10. The parent ion was observed in all the PCB's. The major fragmentation path is loss of successive chlorine atoms from the parent molecule. Each such loss gives a fairly definitive cluster of isotope peaks whose intensity

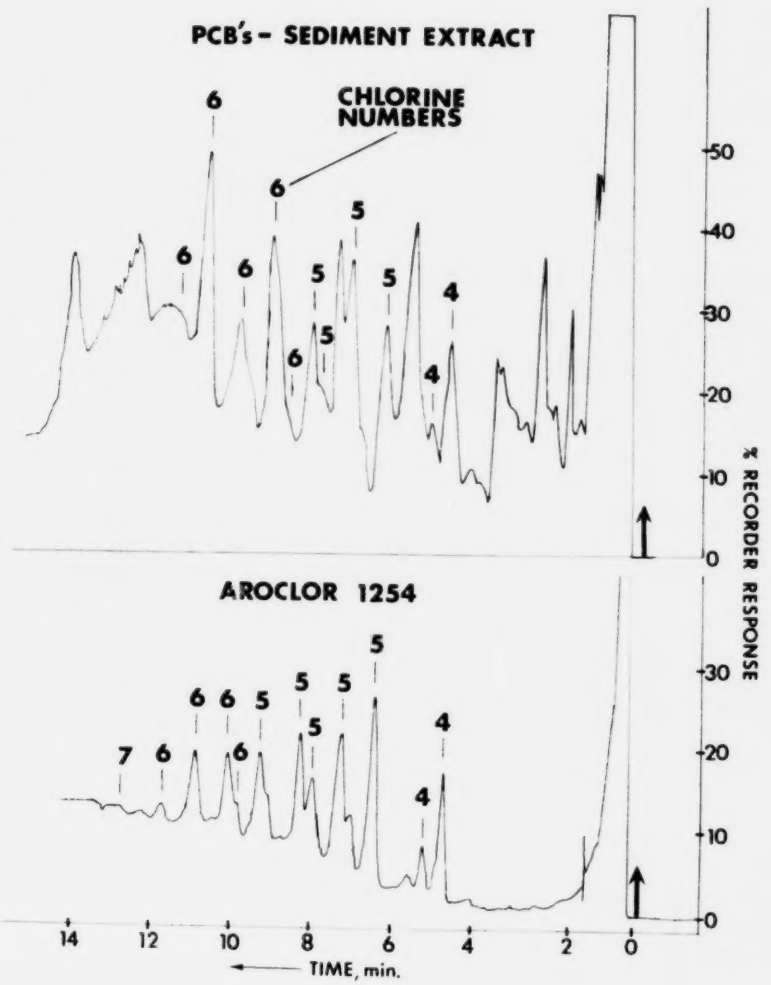


Figure 9. Comparison of the FID Gas Chromatogram of Escambia Bay Sediment Extract with that of Aroclor 1254.

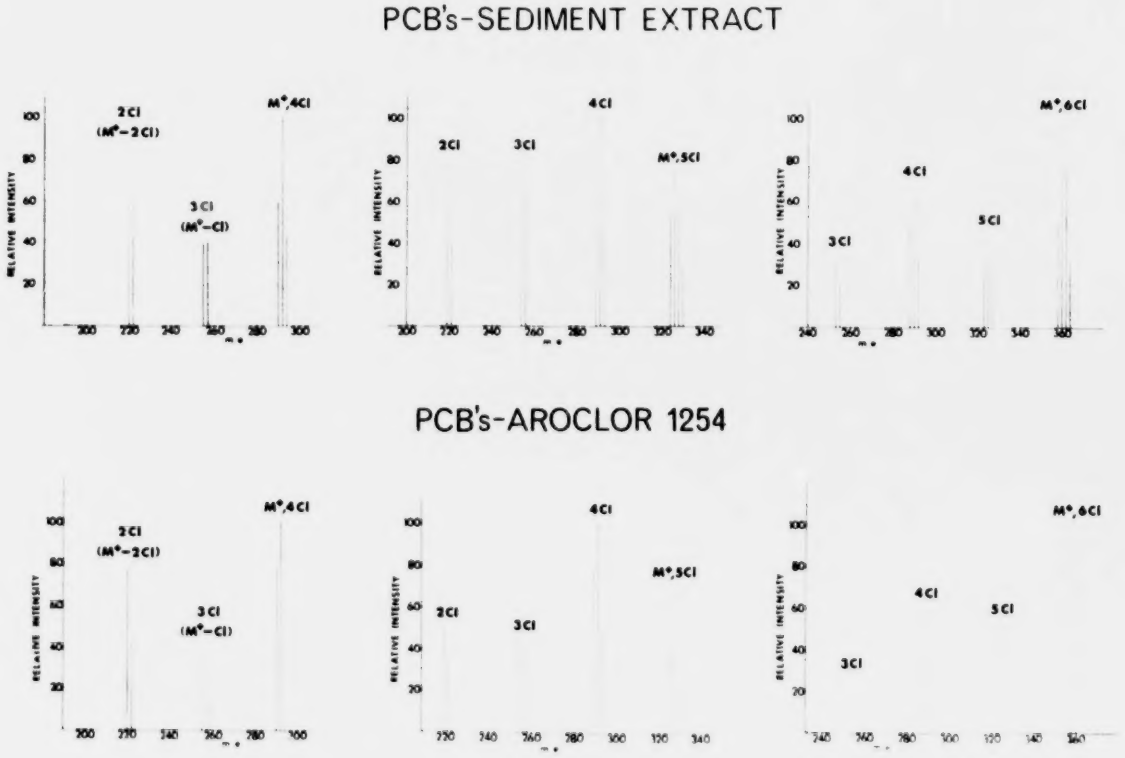


Figure 10. Comparison of Select Chlorine Isotope Clusters from Escambia Bay Sediment Extract with that from Corresponding PCB's in Aroclor 1254

ratios depend upon the number of chlorine atoms left on the fragment. A comparison of the sample and Aroclor standard spectra (Figure 10) shows similar isotope ratios and fragmentation patterns.

Great Miami River, Ohio

Figure 11 shows the GC flame detector chromatogram of a water extract from the Great Miami River in Ohio. Mass spectra of the components eluting from the GC showed 15 of them to be PCB's. They appear to come from a mixture of two Aroclors. The retention time and chlorine numbers of the first eleven of these correspond to an Aroclor 1248 standard, also shown in Figure 11. However, the last four PCB peaks with chlorine numbers of 5, 6, and 7 appear to be from Aroclor 1254 (cf. Figure 9). These four components are in relatively large concentrations, as in the 1254 standard, whereas the standard Aroclor 1248 contains only trace amounts, if any, of 6-chlorine and 7-chlorine PCB's.

Mass spectra showing the clearly definable chlorine isotope clusters of some of the PCB's from the river sample are compared with corresponding spectra from an Aroclor 1248 standard in Figure 12. Only 6 µg of Aroclors were present in the total sample according to electron capture GC analysis. Approximately 0.1 µg of an individual PCB gave a good spectrum.

4. Escambia Bay, Florida Industrial Pollution

The polluted state of the Escambia River and Escambia Bay near Pensacola, Florida, was suspected to be the major cause of numerous fish kills during 1969. The governor of Florida requested technical assistance in evaluating pollution from sources on the river. The NWCCRP was asked to characterize three effluent samples by GC-MS.

The nine compounds identified and confirmed by GC-MS are listed in Table 1 along with five that were tentatively identified. In addition, diphenyl ether, which may be implicated in odor problems and acrylonitrile, were indicated in the Monsanto effluent.

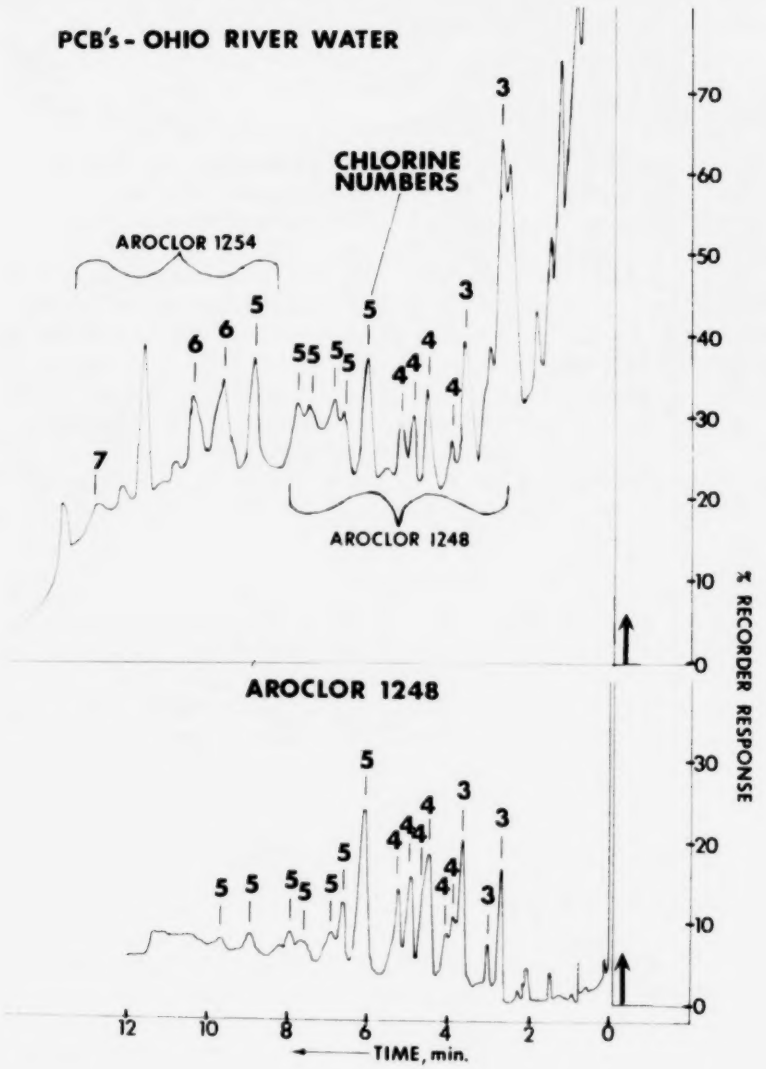


Figure 11. Comparison of the FID Gas Chromatogram of Great Miami River, Ohio Extract with that of Aroclor 1248

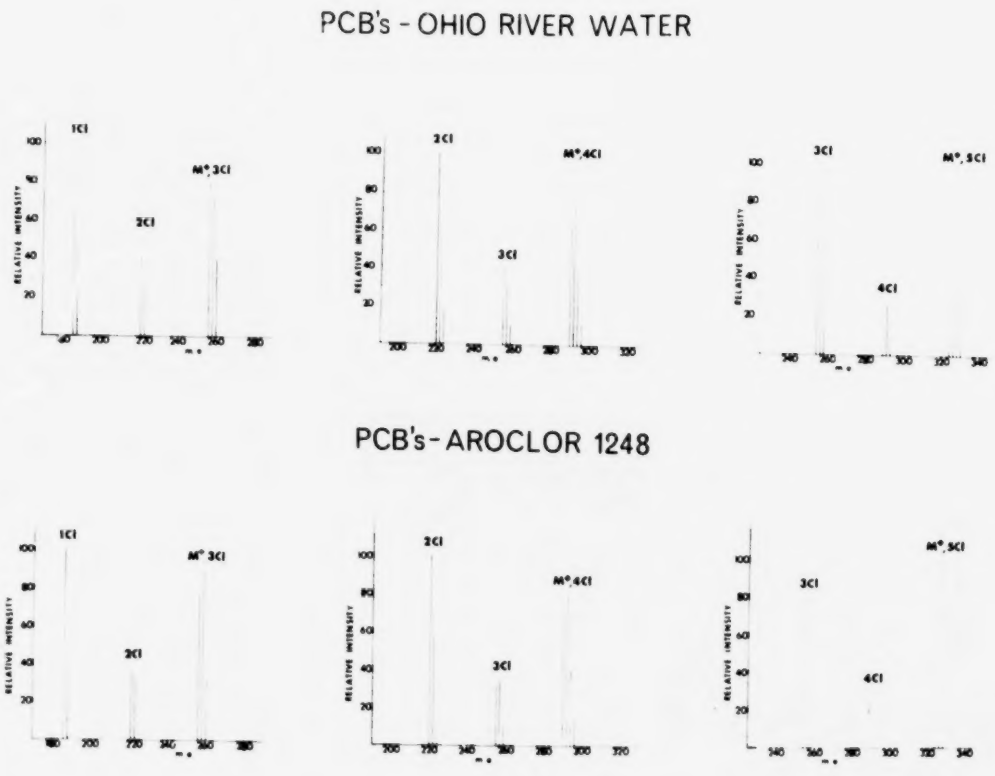


Figure 12. Comparison of Select Chlorine Isotope Clusters from Great Miami River, Ohio Extract with that from Corresponding PCB's in Aroclor 1248

Table 1

Compounds Identified in the Escambia Bay, Florida Industrial Waste Survey

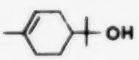
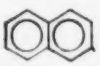
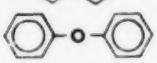
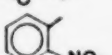
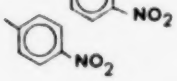
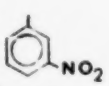
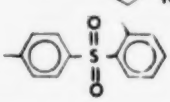
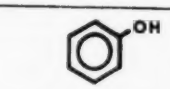
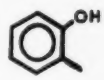
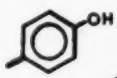
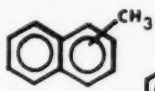
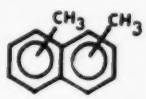
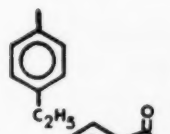
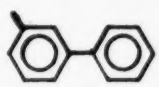
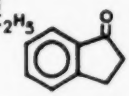
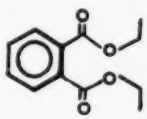
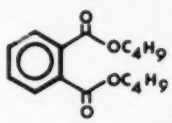
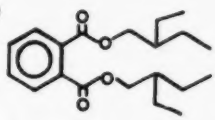
Compound	Structure	Identification confirmed
α-Terpineol		Yes
Naphthalene		Yes
Diphenyl ether		Yes
Dibenzofuran		Yes
o-Nitrotoluene		Yes
p-Nitrotoluene		Yes
Acrylonitrile	CH_2=CH-C≡N	Yes
n-Hexadecane	$C_{16}H_{34}$	Yes
n-Octadecane	$C_{18}H_{38}$	Yes
n-Heptadecane	$C_{17}H_{36}$	No
m-Nitrotoluene		No
2,4'-Dimethyldiphenylsulfone		No
Dibromopropene	(Isomer not determined)	No
2,6-Di-t-butylcresol	(Isomer not determined)	No

Table 2

Compounds Identified in the Kansas City, Kansas Landfill Analysis

Compound	Structure
Phenol	
o-Cresol	
p-Cresol	
Methylnaphthalene	
Dimethylnaphthalene	
1-Methyl-4-ethylbenzene	
3-Methylbiphenyl	
1-Indanone	
Diethyl phthalate	
Di-n-butyl phthalate	
Di-2-ethyl-n-butyl phthalate	
A variety of n-alkanes	$CH_3(CH_2)_nCH_3$

5. *Kansas City Landfill Contaminants*

Many complaints were registered in June, 1969, by citizens of Kansas City, Missouri, concerning a medicinal or "iodine-like" taste in their city water. An investigation was undertaken to determine the source of the contamination. The Kansas City Water Supply Department, monitoring organics at their intake by gas chromatography, showed a heavy organic load in the water.

A suspected source of contamination was a landfill for industrial wastes, recently reopened upstream of the city. Colorimetric tests of extracts of earth and fiberglass samples from the operation proved positive for phenols (compounds that, when chlorinated during water treatment, produce tastes similar to those reported. Results indicated, therefore, that leaching of soil and other materials being bulldozed into the river was the source of the problem.

For corrective action, more positive identification of the contaminants was required. Accordingly, samples of fiberglass from the dump were leached for 30 minutes in distilled water to simulate being pushed into the river. An ether extract of the resulting solution was examined by GC-MS. Positive identification was made of phenol, p-cresol, and benzothiazole.

The Johnson County, Kansas, Water Treatment Plant (Kansas City, Kansas) requested that a similar study for potential pollutants be performed on yet another landfill operation whose drainage could reach their water intake. Should a similar problem occur in their city, such information would permit immediate action.

Among the industries served by the disposal service were a petroleum products plant, a paint company, and several home appliance companies. Examination by GC-MS of extracts of earth, water, and fiberglass indicated the presence of the organic compounds in Table 2 in addition to elemental sulfur.

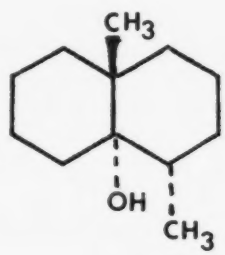
The most interesting compounds from a taste and odor standpoint are phenol, the cresols, and dimethylnaphthalene, which has an odor of burnt rubber and has been

found in the effluent from a refinery's activated sludge plant. Phenol and o- and p-cresol were confirmed by comparison of mass spectra of standards and the sample.

6. *Identification of the Cause of Earthy, Musty Taste and Odor Problems in Ohio Water Supplies*

In March, 1968, the Advanced Waste Treatment Research Laboratory in Cincinnati, Ohio, was requested to conduct studies of an intermittent musty, earthy odor in the Wabash River in Indiana. An investigation showed that the odor was present constantly in Grand Lake, Ohio, the principle headwater of the Wabash River.

In 1929 an earthy odor in water was attributed to actinomycetes (6) and recently a compound with a similar odor, termed "geosmin", was isolated from numerous actinomycetes cultures. Its structure was identified as trans-1,10-dimethyl-trans-9-decalol (V), (7,8). However, GC retention indices showed the river pollutant to be different from "geosmin".



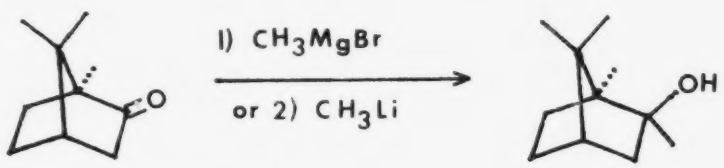
V

Rosen, Mashni, and Safferman of the Advanced Waste Treatment Research Laboratory of the NERC, Cincinnati, Ohio, isolated from a culture of streptomyces lavendulae a compound that matched the odor and gas chromatography retention indexes of the odorous compound from the lake and river samples. It was shown to be different from "geosmin" and was termed "celinol" after the city of Celina, Ohio, which uses Grand Lake as a water supply.

Infrared spectra indicated that the compound was an aliphatic alcohol; high resolution mass spectra and an element map showed a parent ion at mass 168 with an indicated empirical formula of $C_{11}H_{20}O$. The sample, believed to have a structure similar to "geosmin", was submitted to NWCCRP for further structural elucidation.

The NMR spectrum (Figure 13) considered in light of the molecular weight and empirical formula, indicated an aliphatic bicyclic structure. The mass spectrum of "celinol" was compared with those of compounds considered possible on the basis of the above evidence --either a borane or a pinane. The fragmentation pattern was similar to that of isoborneol, but the major fragments were 14 mass units greater (Figure 14) indicative of an added methyl group, which is consistent with the NMR data. The extra methyl group, from NMR evidence, was geminal to the hydroxyl, yielding the structure 2-methylisoborneol (2-exo-hydroxy-2-methyl-bornane).

2-Methylisoborneol had not been reported previously as a naturally occurring compound and no commercial standard was available. We therefore prepared the compound by two different methods: 1) reacting camphor (VI) with methyl magnesium bromide according to Zelinsky (9) and 2) reacting camphor (VI) with methyl lithium reagent.



VI VII

Spectral comparisons (NMR, IR, and MS) confirmed the structure of "celinol" to be identical to 2-methyl-isoborneol (VII). Figure 15 shows the infrared comparison.

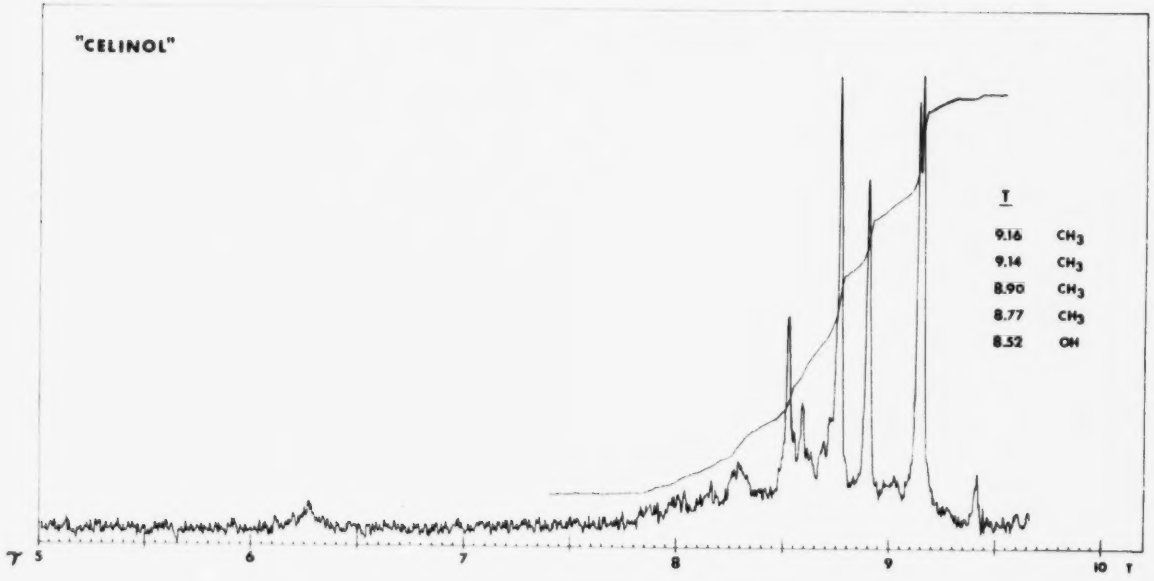


Figure 13. The NMR Spectrum of "Celinol"

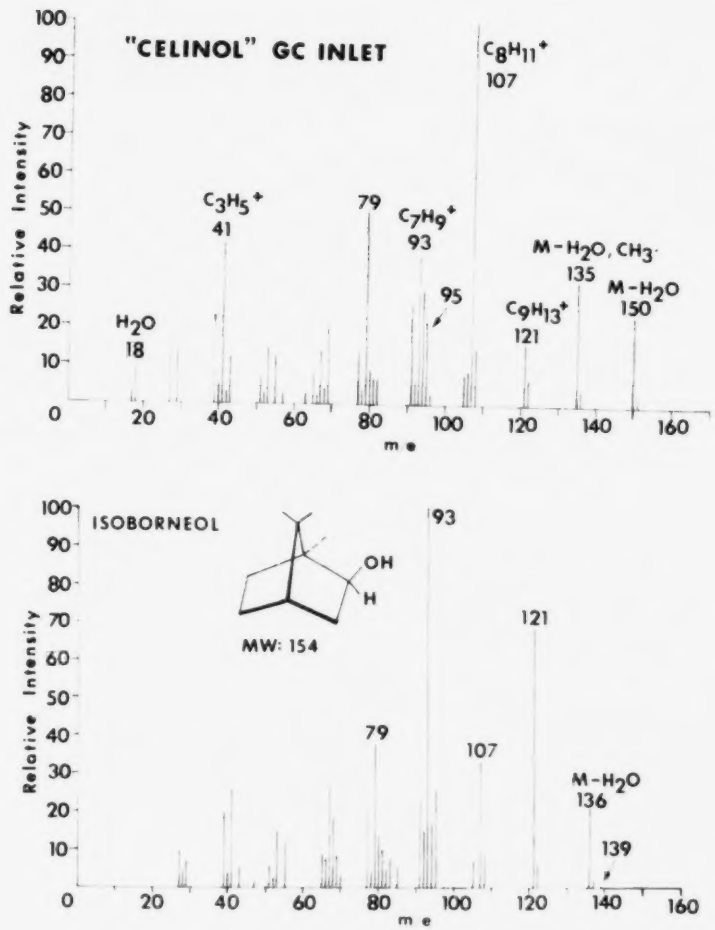


Figure 14. Comparison of the Mass Spectrum of "Celinol" with that of Isoborneol

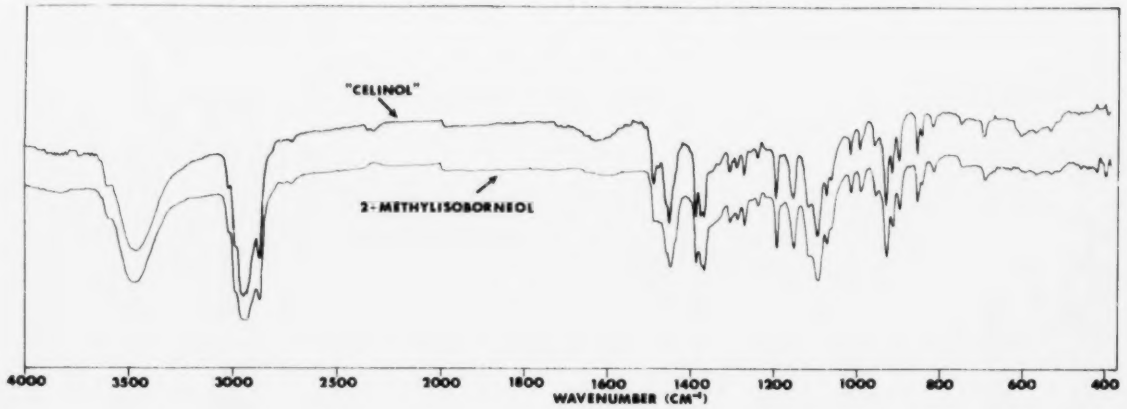


Figure 15. Comparison of the Infrared Spectrum of "Celinol" with that of 2-Methylisoborneol

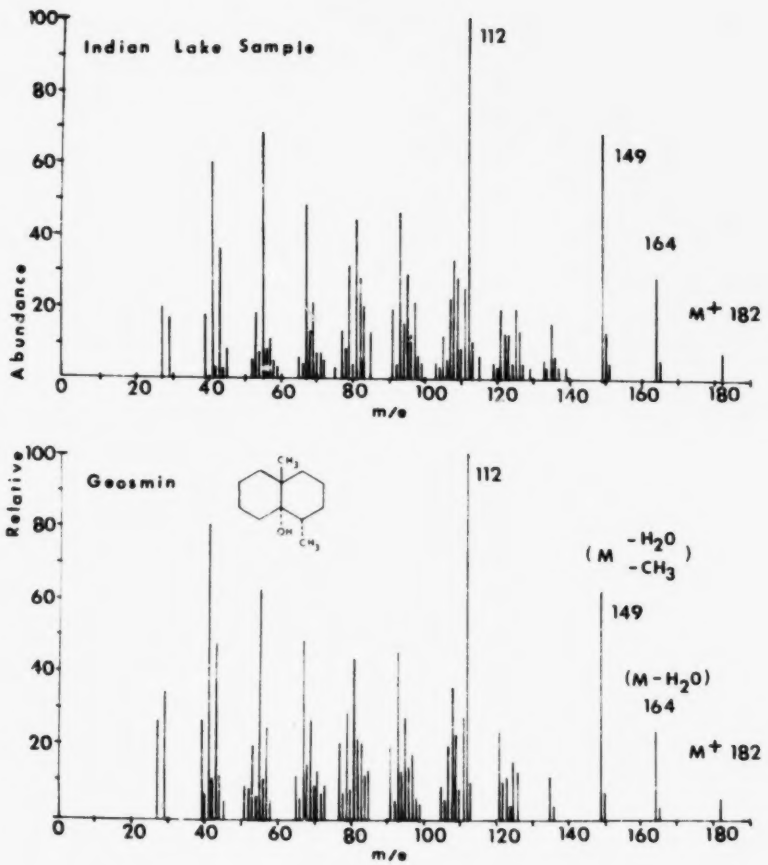


Figure 16. Comparison of the Mass Spectrum of Indian Lake Extract with that of Geosmin

A simultaneous, but independent, investigation of a compound from three other species of actinomycetes by Medsker, Jenkins, and Thomas (10) led to the same structure as "celinol". Further samples from Grand Lake were found to contain both "geosmin" and 2-methylisoborneol. Samples from Indian Lake nearby contained only "geosmin." Figure 16 illustrates the matching of a known sample of "geosmin" with that of an extract from Indian Lake.

The concentration of 2-methylisoborneol and geosmin were estimated by Rosen to be 0.1 ppb and 0.03 ppb, respectively in Grand Lake. The presence of 2-methylisoborneol in a body of natural water had not previously been reported.

Recently Piet, Zoeteman and Kraayeveld, Government Institute for Drinking Water Supply, The Hague, Netherlands, detected "geosmin" and 2-methylisoborneol in rivers of the Netherlands (11).

Having once been identified and associated with a particular problem, a pollutant becomes much more readily identified in future cases. Such an example illustrates an important function of organic contaminants characterization.

7. *Western Louisiana Industrial Waste Survey*

In April, 1971, Dr. T. O. Meiggs, EPA Division of Field Investigations, Denver, Colorado, requested NWCCRP to characterize chemically a number of industrial effluents from an industrialized area in western Louisiana. The information was for an enforcement conference. We identified a total of 50 compounds in 7 different industrial effluents; forty-nine of the identifications were confirmed by comparison of GC-MS data and/or GC retention times of standards with those of the tentatively identified compounds. Some compounds were common to two or more of the effluents.

Values for total organic carbon (TOC), chemical oxygen demand (COD), specific conductivity, and concentrations of total and suspended solids were supplied to the EPA Division of Field Investigations from 24-hour composite samples.

One liter of each of the effluent samples was extracted with chloroform and concentrated. A 50-ft. support coated open tubular (S.C.O.T.) column with carbowax 20M-TPA provided adequate separation of all but one of the mixtures for which a 50 ft. S.C.O.T. column coated with SE-30 was used.

Chemical characterization of these seven industrial effluents

- revealed the discharge of unexpected compounds (not indicated from lists of products and raw materials supplied by the manufacturers) along with other data for enforcement of permit regulations.
- furnished knowledge of treatment effectiveness beyond that provided by gross pollution measurements.
- gave another means of determining the significance of an effluent--whether the compounds present are likely to cause oxygen depletion, to contribute to taste and odor problems or to cause chronic or acute toxic effects in biota.

Petrochemical Company A

Petrochemical Company A, producing olefins and oxygenated hydrocarbons, discharges an estimated 4 million gallons per day. Treatment consists of three ponds connected in series, and covering a total of 5 acres with a 5-6 day retention time. The first and largest of the ponds contains aerators. The third has an overflow structure at the entrance of a bayou into which the effluent is discharged; samples were gathered at this point.

The effluent from Petrochemical Company A contained the most complex mixture of organic compounds (Figure 17). Because no standard was available for comparison, the identification of 3-methylindene rests solely on mass spectrometric data interpretation. All other compounds were confirmed by comparison with standards. Phenol and 2,6-dimethylnaphthalene were found to have the same retention time under the gas chromatographic conditions

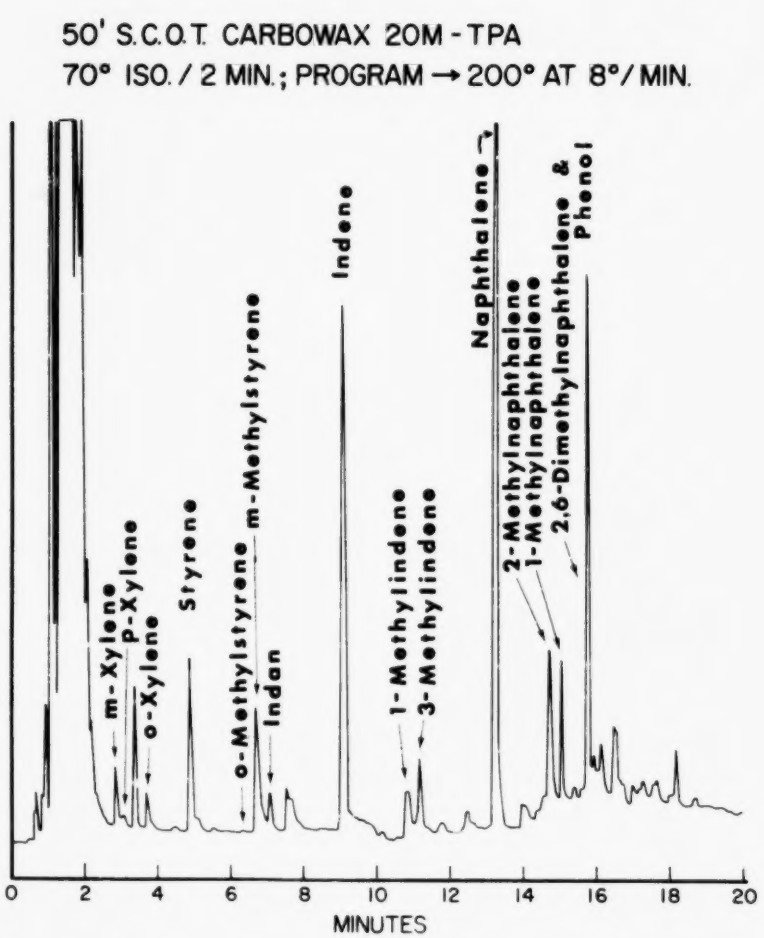


Figure 17. Chemically Characterized Gas Chromatogram of Petrochemical Company "A"

Table 3

Chemical Characterization and Gross Pollution Measurements of Petrochemical Company A

GROSS POLLUTION MEASUREMENTS

Total Organic Carbon	180 mg/ℓ
Chemical Oxygen Demand	612 mg/ℓ
Total Solids	868 mg/ℓ
Suspended Solids	78 mg/ℓ
Specific Conductivity	1,100 μ mhos/cm

CHEMICAL CHARACTERIZATION

Products	Raw Materials	Compounds Identified	Approximate Concentration (mg/ℓ)	Approximate Discharge (lbs/day)
Propylene	Raw gas	m-Xylene	0.008	0.3
Ethylene	Ethane	p-Xylene	0.002	0.1
Butadiene	Refinery gases	o-Xylene	0.006	0.2
Butane	Refinery C_2 stream	Styrene	0.031	1.1
Octane		o-Methylstyrene	0.001	0.1
Ethylene glycol	Refinery C_3 stream	Indane	0.007	0.3
Ethylene oxide		Indene	0.026	0.9
Polyglycols	Propane	Methylindene	0.002	0.1
Ammonia	Butadiene	3-Methylindene	0.003	0.1
	Nitrogen	Naphthalene	0.053	1.9
	Hydroformer gas	2-Methylnaphthalene	0.030	1.1
	Platformer gas	1-Methylnaphthalene	0.025	0.9
		2,6-Dimethylnaphthalene	0.015	0.5
		Phenol	0.060	2.1

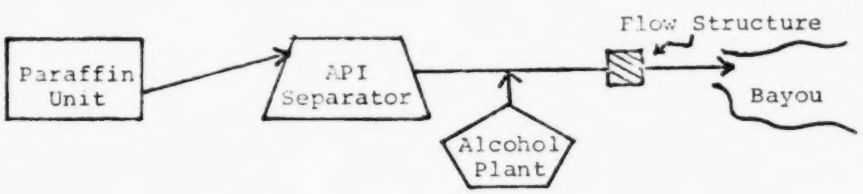
employed, but the mass spectrometric fragmentation patterns of each were readily discernable even though they were present as a mixture. A mixture of two standards confirmed the spectral interpretation.

Sulfur and several polycyclic aromatics such as indenes and naphthalenes have been cited as the source of odor in oil products (12). They may therefore be responsible for odor problems in drinking water supplies derived from sources into which petroleum by-products are discharged as waste.

Table 3 presents a summary of the gross pollution parameters and a list of products and raw materials supplied by the company, along with the identified compounds, their approximate concentrations, and their rates of discharge. A comparison of the list of products and raw materials with that of the identified compounds illustrates an important point--the lists supplied by a company cannot be used exclusively as a key for the identification of organic pollutants in industrial discharge.

Petrochemical Company B

The second petrochemical plant, producing alcohols and paraffins, discharges about 314 million gallons per day. Wastes from a paraffin unit and an alcohol unit enter a ditch at two points and pass through a "flow structure" before emptying into a bayou. The effluent from the paraffin unit passes through an American Petroleum Institute (API) separator before entering the ditch; the effluent from the alcohol unit, comprising about 80% of the total effluent, is not treated. The sample from the ditch was taken after the effluent passed through the "flow structure."

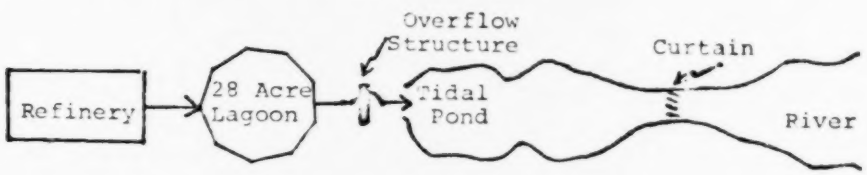


Only normal short chain alcohols with even carbon numbers were found to any appreciable extent. n-Hexanol was present in the largest concentration along with lesser amounts of n-butanol and n-octanol and a trace of n-decanol (Figure 18). The absence of any traces of paraffinic hydrocarbons in the effluent is conspicuous. Either the API separator did an efficient job of removing them or their large molecular weight prevented their elution from the chromatographic column. Dilution by the effluent from the alcohol unit would also help mask their presence if they were being discharged in small amounts.

The gross pollution measurements and chemical characterization data are summarized in Table 4.

Petrorefinery Company A

The first of the two refineries studied discharges an estimated 3 million gallons per day and produces about 230,000 barrels per day. Treatment consists of a simple 8-hour retention-time lagoon that discharges through an overflow structure into a tidal pond of a river. To avoid tidal influences, sampling was done at the lagoon overflow structure.



The chloroform extractables of the effluent consisted primarily of phenol, o-cresol, and normal long chain aliphatic hydrocarbons (Figure 19). Undecane (C_{11}) through nonadecane (C_{19}) were identified and confirmed. Small amounts of unspecified branched isomers appear between the peaks of these normal hydrocarbons. Although both 1-methylnaphthalene and 2-methylnaphthalene were present, no naphthalene was detected in measurable concentration. The gross pollution measurements and chemical characterizations are presented in Table 5.

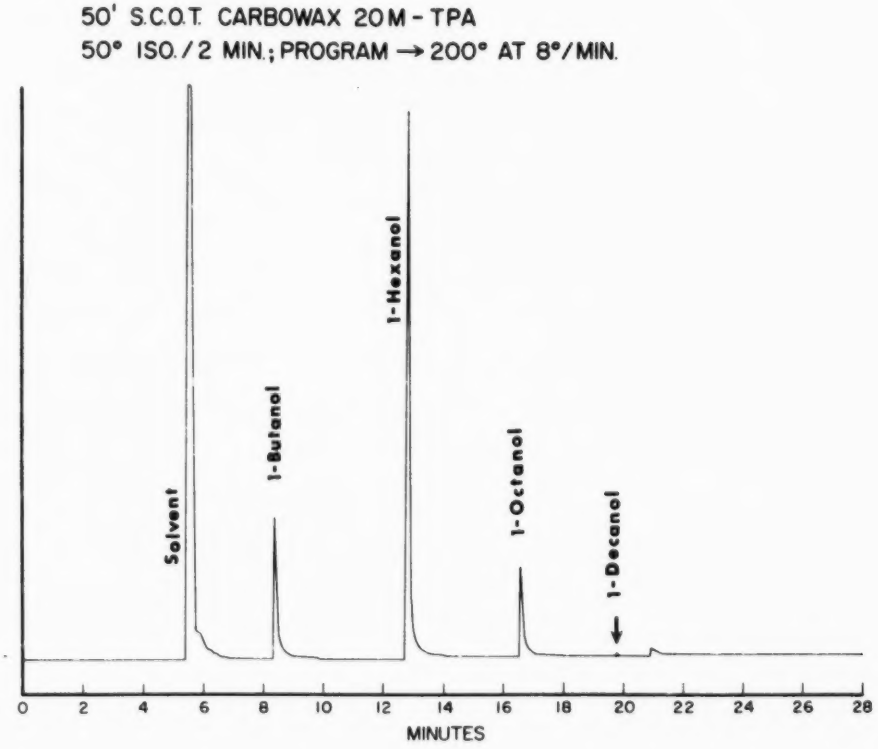


Figure 18. Chemically Characterized Gas Chromatogram of Petrochemical Company "B"

Table 4

Gross Pollution Measurements and Chemical Characterization of Petrochemical Company B

GROSS POLLUTION MEASUREMENTS

Total Organic Carbon	130 mg/ℓ
Chemical Oxygen Demand	Not available
Total Solids	2650 mg/ℓ
Suspended Solids	34 mg/ℓ
Specific Conductivity	4,000 μ mhos/cm

CHEMICAL CHARACTERIZATION

Products	Raw Materials	Compounds Identified	Approximate Concentration (mg/ℓ)	Approximate Discharge (lbs/day)
Normal paraffin	Ethylene	1-Butanol	16.0	90
Industrial alcohols	Aluminum	1-Hexanol	65.0	375
Ethylene	Hydrogen	1-Octanol	19.0	110
Methyl chloride	Raffinate	1-Decanol	2.5	15
Ethoxylates	Sulfuric acid			
	Ethylene oxide			
	Acetic acid			
	Caustic			
	Phosphoric acid			
	Kerosene			
	Ethane			
	Propane			
	Methanol			
	HCl			

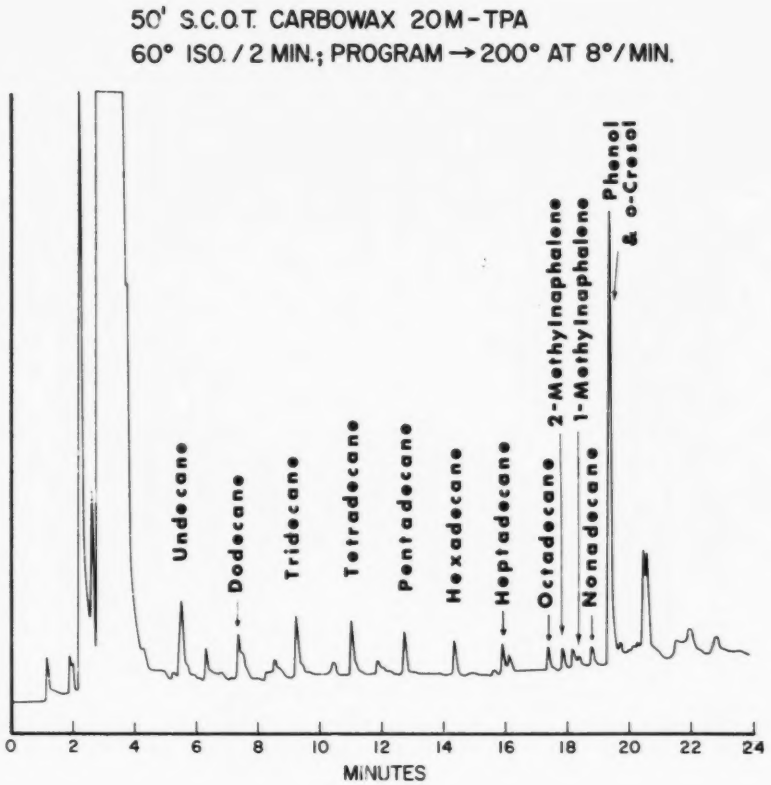


Figure 19. Chemically Characterized Gas Chromatogram of Petrorefinery "A"

Table 5

Gross Pollution Measurements and Chemical Characterization of Petrorefinery Company "A"

GROSS POLLUTION MEASUREMENTS

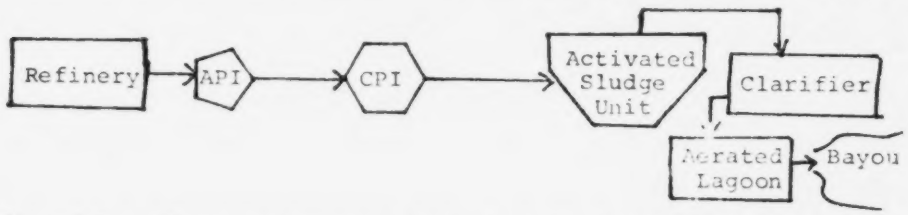
Total Organic Carbon	15 mg/ℓ
Chemical Oxygen Demand	Not available
Total Solids	9,220 mg/ℓ
Suspended Solids	38 mg/ℓ
Specific Conductivity	13,700 μ mhos/cm

CHEMICAL CHARACTERIZATION

Products	Raw Materials	Compounds Identified	Approximate Concentration (mg/ℓ)	Approximate Discharge (lbs/day)
LPG propane	Crude oil	Undecane	0.027	69
Propylene	Excess gas oil	Dodecane	0.031	79
Orthoxylene	Extracts	Tridecane	0.042	107
Aromatics		Tetradecane	0.039	99
		Pentadecane	0.030	76
		Hexadecane	0.026	66
		Heptadecane	0.022	53
		Octadecane	0.017	43
		Nonadecane	0.013	33
		2-Methylnaphthalene	0.013	33
		1-Methylnaphthalene	0.005	12
		Phenol	0.200	510
		o-Cresol	0.120	300

Petrorefinery Company B

The treatment facilities of refinery B, which discharges about 1 million gallons per day and produces about 70,000 barrels per day, are more extensive than those of Company A. The effluent from the refinery flows through an API separator and a corrugated plate interceptor (CPI) into an activated sludge unit. It then passes through a clarifier into a 24-hour retention-time aerated lagoon from which it discharges into a bayou.



The chloroform extractables of the effluent produced a chromatogram resembling that of a crude oil and mass spectra characteristic of only aliphatic hydrocarbons. The normal chain hydrocarbons were present in larger amounts than the many branched isomers and thus stood out as spikes superimposed upon a base of complex, poorly resolved lumps in the gas chromatograph (Figure 20). Undecane (C_{11}) through heineicosane (C_{21}) were confirmed. No phenols or naphthalenes were identified in this sample. The gross pollution measurements and chemical characterizations are summarized in Table 6.

Synthetic Rubber Company

A synthetic rubber company discharges about 6 million gallons per day with only primary treatment followed by discharge via a drainage ditch to a bayou.

Styrene (one of the 3 raw materials listed), furfural, and 1-methylnaphthalene were identified and confirmed in the effluent. The compound producing the largest peak in the gas chromatogram (Figure 21) and four isomers of apparent molecular weight 156 could not be identified from their mass spectra alone; lack of time and manpower precluded further investigation. Table 7 summarizes the results of the analysis.

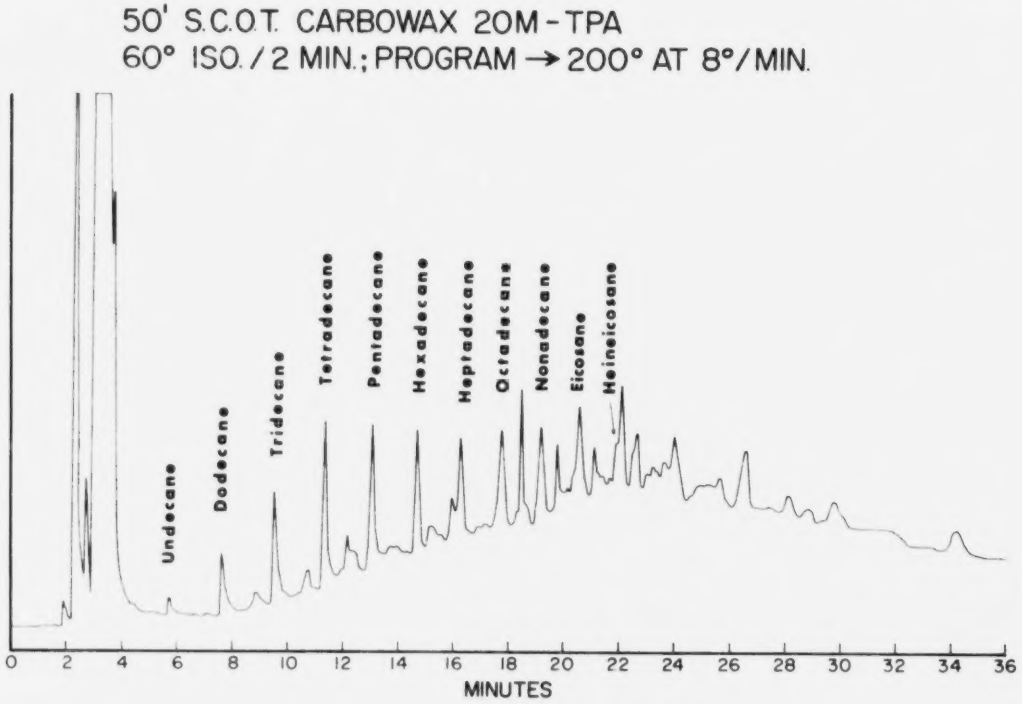


Figure 20. Chemically Characterized Gas Chromatogram of Petrorefinery Company "B"

Table 6

Gross Pollution Measurements and Chemical Characterizations
of Petrorefinery Company "B"

GROSS POLLUTION MEASUREMENTS

Total Organic Carbon	210 mg/ℓ
Chemical Oxygen Demand	676 mg/ℓ
Total Solids	2430 mg/ℓ
Suspended Solids	182 mg/ℓ
Specific Conductivity	3900 μ mhos/cm

CHEMICAL CHARACTERIZATIONS

Products	Raw Materials	Compounds Identified	Approximate Concentration (mg/ℓ)	Approximate Discharge (lbs/day)
LPG	Crude oil	Undecane	0.05	0.4
Propane	Isobutane	Dodecane	0.22	2.2
Butane	PVC	Tridecane	0.39	3.8
Gasoline		Tetradecane	0.58	5.6
Kerosene		Pentadecane	0.49	4.8
Diesel fuel		Hexadecane	0.42	4.0
Heating oil		Heptadecane	0.34	3.3
#6 Fuel oil		Octadecane	0.33	3.2
Coke		Nonadecane	0.31	3.0
		Eicosane	0.30	2.9
		Heineicosane	0.19	1.8

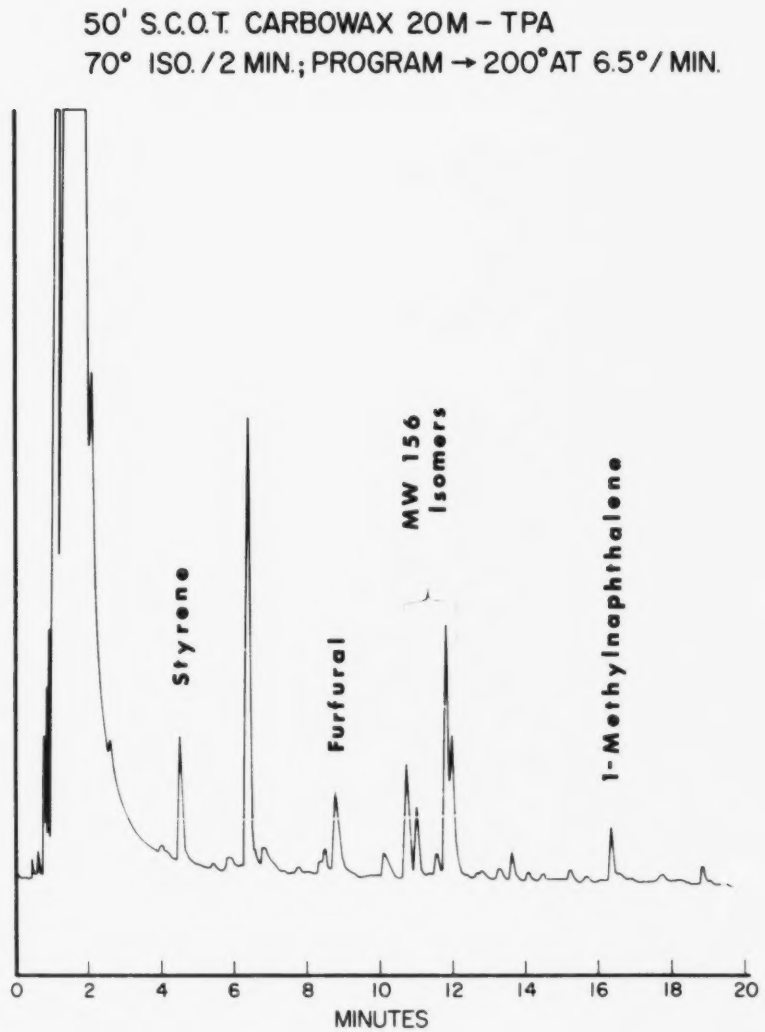


Figure 21. Chemically Characterized Gas Chromatogram of Synthetic Rubber Company

Table 7

Gross Pollution Measurements and Chemical Characterization of Synthetic Rubber Company

GROSS POLLUTION MEASUREMENTS

Total Organic Carbon	52 mg/ℓ
Chemical Oxygen Demand	168 mg/ℓ
Total Solids	3210 mg/ℓ
Suspended Solids	76 mg/ℓ
Specific Conductivity	5000 μ mhos/cm

CHEMICAL CHARACTERIZATION

Products	Raw Materials	Compounds Identified	Approximate Concentration (mg/ℓ)	Approximate Discharge (lbs/day)
Synthetic rubber	Butadiene	Styrene	0.0026	1.3
	Styrene	Furfural	0.0017	0.9
	Carbon black	1-Methylnaphthalene	0.0017	0.9

Chemical Company A

Chemical Company A, a producer of chlorinated hydrocarbons discharges about 4 million gallons of effluent per day from their organics plant into a ditch. Its treatment, after mixing with the effluent from a caustic and chlorine unit, consists only of dilution with cooling water before discharge into a river.

1,1,2-Trichloroethane and 1,1,2,2-tetrachloroethane were identified as the two main contaminants (Figure 22). The total discharge at the above mentioned rate amounted to over 300 pounds of these chlorinated hydrocarbons per day. Table 8 summarizes the findings.

Chemical Company B

The second chemical company, a polymer producer, discharges an estimated 2 million gallons of effluent per day. The treatment consists of a series of six lagoons, with a 4-5 day total retention, that discharge into a river. The only two compounds of significant amount, as determined by gas chromatography, were identified as decane and undecane (Figure 23). No gross pollution measurements were available. Table 9 summarizes the findings.

8. Color Body Characterization and Related Studies from a Kraft Paper Mill Effluent

The Interstate Paper Company at Riceboro, Georgia, utilizes a recently developed lime treatment process to remove "color bodies" from the effluent of Kraft pulp mills. The lime treatment removes 80-90% of the color from the effluent; however, during passage through the stabilization lagoon, the water becomes colored again. Because of the unusually long retention time of the lagoon (3-6 months) the reappearance of the color may result from one or both of two processes: 1) decomposition of previously uncolored compounds that were not removed by lime treatment and 2) leaching of naturally occurring "color bodies" present in the soil at the bottom of the lagoon. The waste treatment system is presented below.

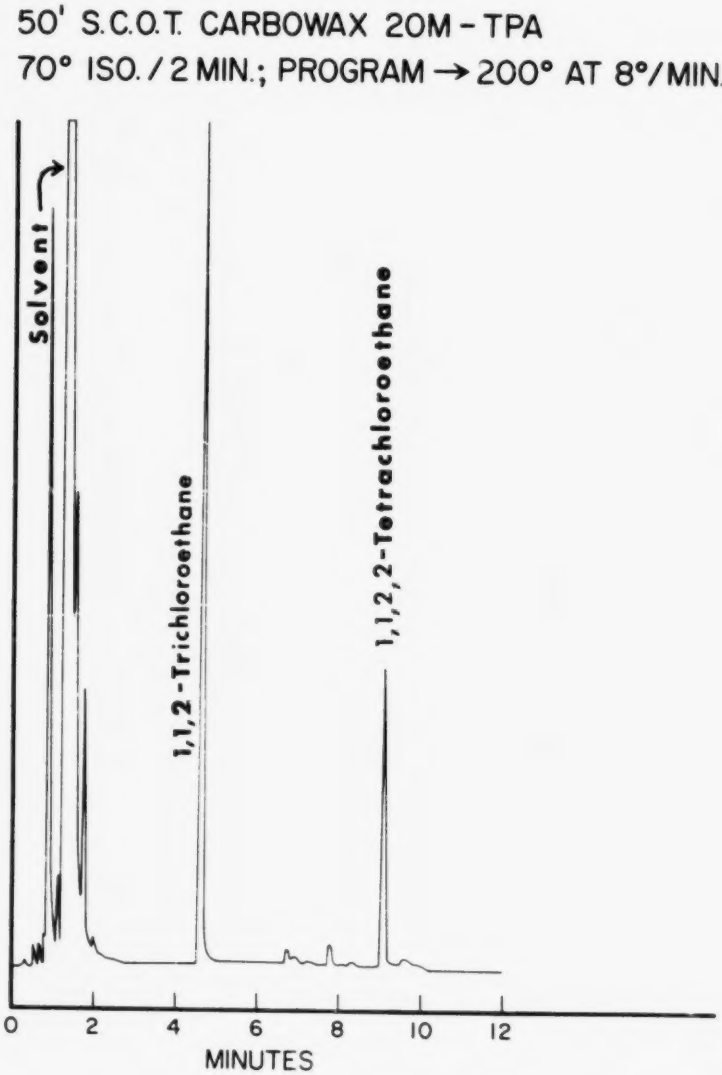


Figure 22. Chemically Characterized Gas Chromatogram of Chemical Company "A"

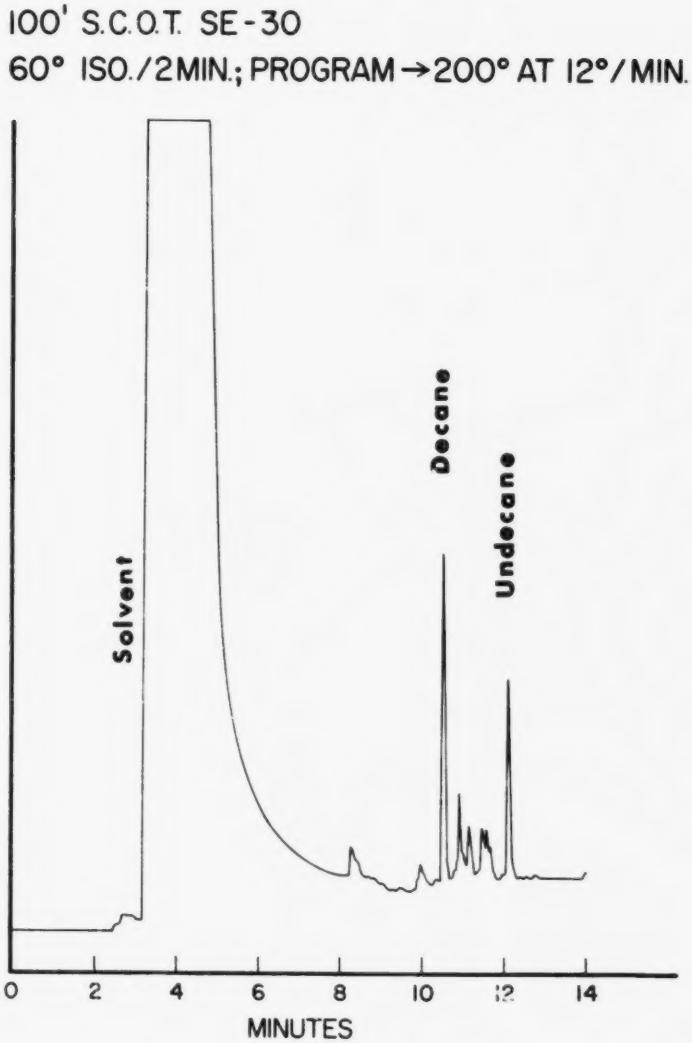


Figure 23. Chemically Characterized Gas Chromatogram of Chemical Company "B"

Table 8

Chemical Characterization of Chemical Company A

Products	Raw Materials	Compounds Identified	Approximate Concentration (mg/ℓ)	Approximate Discharge (lbs/day)
Chlorine	Sodium chloride	1,1,2-Trichloroethane	5.4	240
Caustic soda	Ethylene	1,1,2,2-Tetrachloroethane	2.2	95
Aliphatics				
Chlorinated hydrocarbons				
Silica pigments				
Sodium chloride				
HCl				

Table 9

Chemical Characterization of Chemical Company B

Products	Raw Materials	Compounds Identified	Approximate Concentration (mg/ℓ)	Approximate Discharge (lbs/day)
Polyolefins	Ethylene	Decane	0.03	0.6
Polyethylene	Propylene	Undecane	0.02	0.4
Polypropylene	Alcohol			
	Aluminum alkyls			
	Titanium chloride			

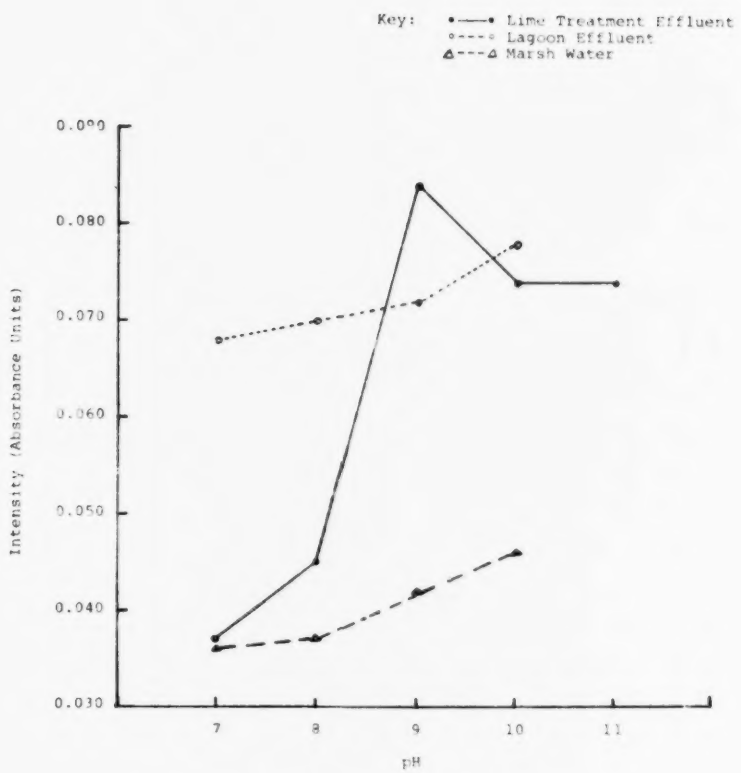
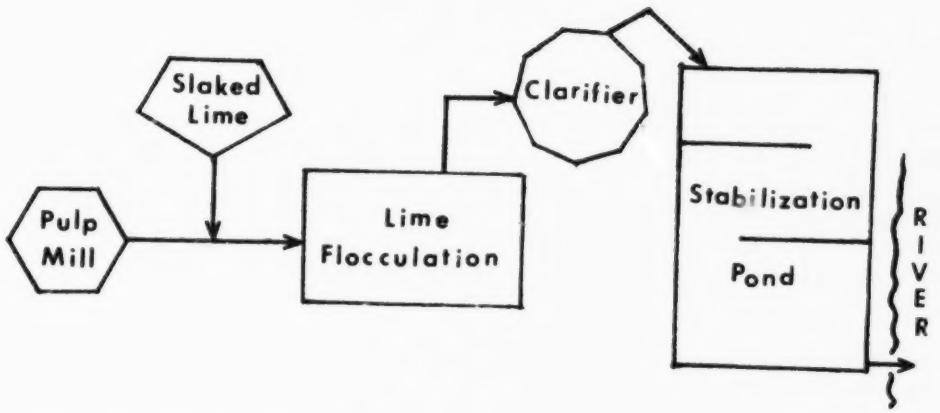


Figure 24. Comparison of Kraft Pulp Mill Effluent and Marsh Water Color Intensity as a Function of pH



Some physical characteristics of the lagoon effluent were compared with those of nearby marsh water and of the effluent following lime treatment. Plots of color intensity at 430 nm as a function of pH for the three samples are shown in Figure 24. The curve for the lagoon effluent parallels the curve for marsh water but differs greatly from that of the effluent following lime treatment. Fluorescence spectra were recorded for each sample, both without any pH adjustment and after acidification to pH 2 with HCl. The wavelengths of the fluorescence maxima and their intensities relative to that of the lagoon effluent are given in Table 10.

Table 10

Comparison of Kraft Pulp Mill Effluent and Marsh Water Fluorescent Spectra

Sample	Fluorescence Maxima	Intensity Ratio
Lime treatment effluent	427 nm	3.8
Lagoon effluent	450 nm	1.0
Marsh water	450 nm	1.8
After Acidification		
Lime treatment effluent	390 nm	1.4
Lagoon effluent	450 nm	1.0
Marsh water	450 nm	1.7

The absorption and fluorescence data indicate that the color characteristics of the lagoon sample closely resemble those of the marsh water.

Two further experiments were performed to determine the source of the color bodies. One liter of lime-treated effluent was sparged with air for 120 days to test for the presence of compounds capable of decomposing to colored products. During that time, however, the color decreased probably because of a change in pH caused by CO_2 absorption.

In addition, mud from the lagoon bottom was dried, powdered, and then leached with calcium hydroxide solutions of two different concentrations. The 5-gram mud samples were shaken with 100 ml of solution for 10 days. Absorption measurements at 420 nm were made after 5 and 10 days. The data summarized in Table 11 indicate that the leaching of color from the soil is pH dependent.

Table 11

Color Leached from Lagoon Mud as a Function of Calcium Hydroxide Concentration

Solution	Absorbance at 420 nm	
	5 days	10 days
H_2O	0.117	0.142
10^{-4}M $Ca(OH)_2$	0.124	0.136
10^{-3}M $Ca(OH)_2$	0.181	0.182

As a result of the study, the color increase in the lagoon effluent was attributed to the leaching action of the alkaline waste from the lime treatment.

An effort was made to identify the compounds responsible for the color in the effluent. Freeze concentration followed by gel permeation chromatography of the

lagoon effluent yielded molecular weight values for the "color bodies" of 2,500 to 5,000. Further work on the molecular weight characteristics of these samples is being conducted in detail by the Institute for Paper Chemistry under FWQA Contract 1240-DKO.

The amount of acid-insoluble organic matter is relevant to the color body determination since lignin and other color-producing large molecules can be precipitated from pulp mill effluents by acidification. The difference between the total organic carbon (TOC) contents of a sample before and after acidification gives an indication of the concentration of acid-insoluble organics. Such measurements made on the pulp mill effluent both before and after lime treatment (refer to Table 12) show that most of the acid-insoluble components are removed by the treatment.

Table 12

Comparison of the Amounts of Acid Insoluble Organics in the Lime Treated and the Untreated Effluent Samples

Sample	TOC Before Acidification	TOC After Acidification (pH 1)	Acidification Insolubles
Lime (Treated)	117 mg/l	111 mg/l	5%
Untreated	216 mg/l	112 mg/l	48%

Analyses of effluent samples from before and after lime treatment and after lagooning were made to determine the effect of the treatment on the organic wastes discharged. (The technique is described in references 13 and 14.) Each sample was made basic to pH 11.5 and extracted with chloroform to remove the neutral volatiles. The extracts were concentrated and analyzed by gas chromatography-mass spectrometry. A list of the compounds identified is presented in Table 13.

Table 13

Compounds Tentatively Identified in the
Neutral Volatiles Fraction of the
Riceboro Pulp Mill Effluent

p-cymene
limonene
guaiacol
a menthene isomer
1-methoxy-4-(1-propenyl)-benzene
1-methoxy-4-pentylbenzene

The aqueous residue was methylated with dimethyl sulfate and re-extracted with chloroform. GC-MS analysis of the extract after concentration yielded the compounds listed in Table 14.

Table 14

Compounds Tentatively Identified in the
Phenols and Acids Fraction of the
Riceboro Pulp Mill Effluent

dimethylsulfone
2,5-diethylthiophene
4-methoxybenzaldehyde
3,4-dimethoxyethylbenzene
p-methoxypropiophenone
3,4-dimethoxybenzaldehyde
3,4-dimethoxyacetophenone
3,4,5-trimethoxyacetophenone
methyl 3,4-dimethoxybenzoate
3,4-dimethoxypropiophenone
methyl pimarate
methyl isopimarate
methyl abietate
methyl dehydroabietate

The results of this analysis indicated that

- most of the neutral volatiles were not affected by lime treatment.
- most of the resin acids are significantly diminished in concentration after lime treatment.

9. *Characterization of Foam from Kraft Pulp Mills*

Source of an Environmental Contamination

Brown foam, floating to shore in masses, has presented a persistent problem in Perdido Bay in Florida's western panhandle. Tall oil in the discharge from a kraft paper mill at the north of the bay was suspected to be the cause of the foam.

Three samples were collected and analyzed. The first, a water sample, was taken from below the second of 2 sedimentation ponds in a stream composed almost totally of the plant's effluent. A foam and scum sample was collected in Perdido Bay about 17 miles below the mill at a point where the foam was in abundance. The last sample was of foam only and was taken from a point about 24 miles below the papermill.

To determine the presence of resin acids and fatty acids, the samples were acidified, extracted with chloroform, esterified with diazomethane, and analyzed by flame ionization gas chromatography. Structures were confirmed by GC-MS. The compounds listed in Table 15 were identified (the acids as the methyl esters) for the three samples.

The identification of the same and similar compounds in all three samples indicates that the paper mill is the source of the foam contamination in the bay. The mill has begun installing secondary treatment. In-plant changes have reduced the organic content of the effluent to one-third of its former load.

Table 15

Compounds Identified in Perdido Bay Kraft Papermill Wastewater, Foam, and Scum Samples

Mill Wastewater	Foam & Scum (17 miles below mill)	Foam (24 miles below mill)
Pimaric acid	Pimaric acid	Pimaric acid
Isopimaric acid	Isopimaric acid	Isopimaric acid
Dehydroabietic acid	Dehydroabietic acid	Dehydroabietic acid
6,8,11,13-Abietatetraen-18-oate	6,8,11,13-Abietatetraen-18-oate	6,8,11,13-Abietatetrean-18-oate
Unidentified resin acid	Unidentified resin acid	Unidentified resin acid
---	Unidentified resin acid	Unidentified resin acid
Palmitic acid	---	Palmitic acid
Stearic acid	Stearic acid	Stearic acid
---	Eicosanoic acid	Eicosanoic acid
Lignoceric acid	Lignoceric acid	---

Constituents from a Bleach Stage Caustic Clarifier

The International Paper Company at Springhill, Louisiana, was involved in developing a "massive lime process" to remove color from the effluent of the "bleach plant caustic stage." After the lime was added to the effluent and the mixture was passed to a "caustic clarifier", however, excessive foaming developed that caused flow stoppage and solids carry-over. Identification of the foam constituents was desired in order to take action to reduce the foaming.

The analytical procedure was similar to previous characterization of paper mill effluents (13,14). The foam was mixed with distilled water in a separatory funnel and made strongly alkaline with sodium hydroxide. The chloroform extracts of the basic solution contained the neutral volatile constituents which were only minor components of the mixture and were not examined further.

The acidic fraction in the aqueous phase, comprising the majority of the organic componnents, was methylated by two procedures to produce derivatives that could be separated by gas chromatography. Methylation of the chloroform extract of the acidified aqueous phase by diazomethane proved superior to direct methylation with dimethyl sulfate; the amounts of methyl esters were greater using the former method.

A GC-MS analysis showed no resin acid or phenolic compounds in detectable amounts, in contrast to previous studies involving total effluents. Instead, the foam consisted primarily of long-chain carboxylic ("fatty") acids. Palmitic and stearic acids were in predominance (Figure 25). Also present in significant amounts were identified isomers of the di- and triunsaturated analogs of octadecanoic acid. The identifications of the numbered peaks in Figure 25 are listed below:

Peak Number	Methyl Ester of
1	heptanoic acid (heptylic acid)
2	octanoic acid (caprylic acid)
3	nonanoic acid (pelargonic acid)
4	decanoic acid (capric acid)
5	undecanoic acid
6	dodecanoic acid (lauric acid)

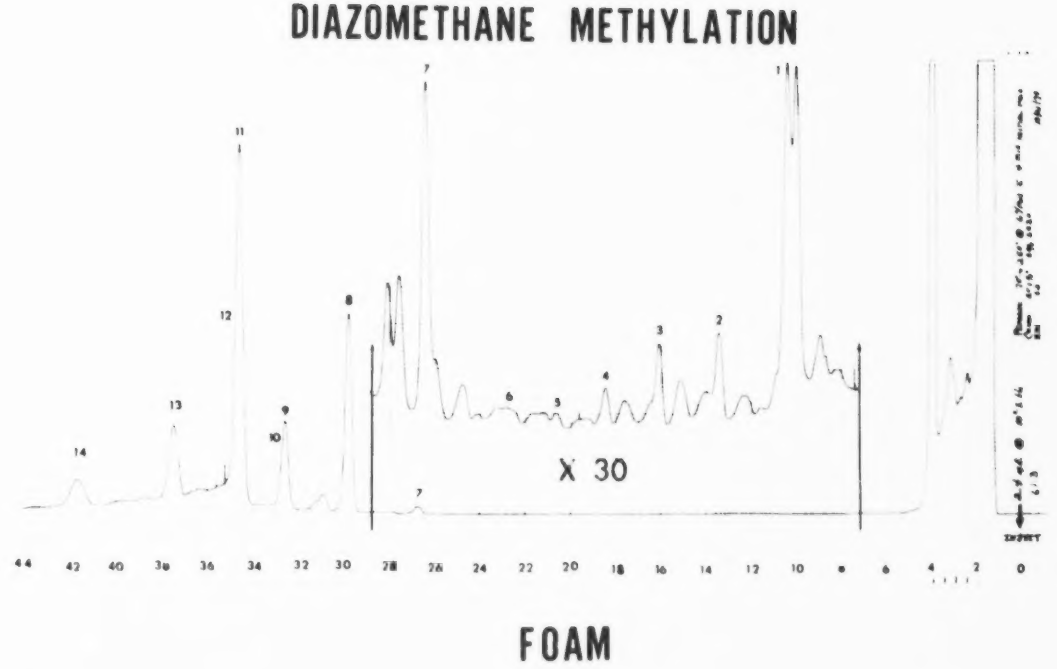


Figure 25. Chemically Characterized Gas Chromatogram of Foam from a Kraft Papermill Bleach Stage Caustic Clarifier

Peak Number	Methyl Ester of
7	tetradecanoic acid (myristic acid)
8	hexadecanoic acid (palmitic acid)
9	octadecanoic acid (stearic acid)
10	diunsaturated analog of octadecanoic acid
11	unidentified ester; molecular weight 262
12	unidentified ester; molecular weight 280

A mechanical means of foam control was tried; however, the plant was closed down for lack of funds and no chemical solution to the problem was attempted.

10. Analysis of Oil Spills by NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a useful method for helping to determine the source of an oil spill. NMR can rapidly distinguish between different types of oils and sometimes can identify the type of oil in a spill without reference to a standard. Its greatest disadvantage is that it cannot distinguish between different oils of the same general type.

Shell Point Beach Oil Spill

An oil spill occurred in February, 1969, off the coast of St. Mark, Florida, on Shell Point Beach. The U. S. Coast Guard collected samples from a nearby punctured barge and from Shell Point Beach 3, 5, and 7 days after the spill was noticed. An analysis was performed in conjunction with the Chemical Services Branch to determine whether the barge was the source of the spill.

A small amount of each sample was dissolved in carbon tetrachloride containing 2-3% tetramethylsilane as a reference standard. The NMR spectra were scanned and electronic integrals of the areas under each signal in the spectra were made in triplicate (Figure 26). Since each sample was run at least three times, the mean signal areas are averages of at least nine integrals. The average areas under the signals were normalized (Table 16).

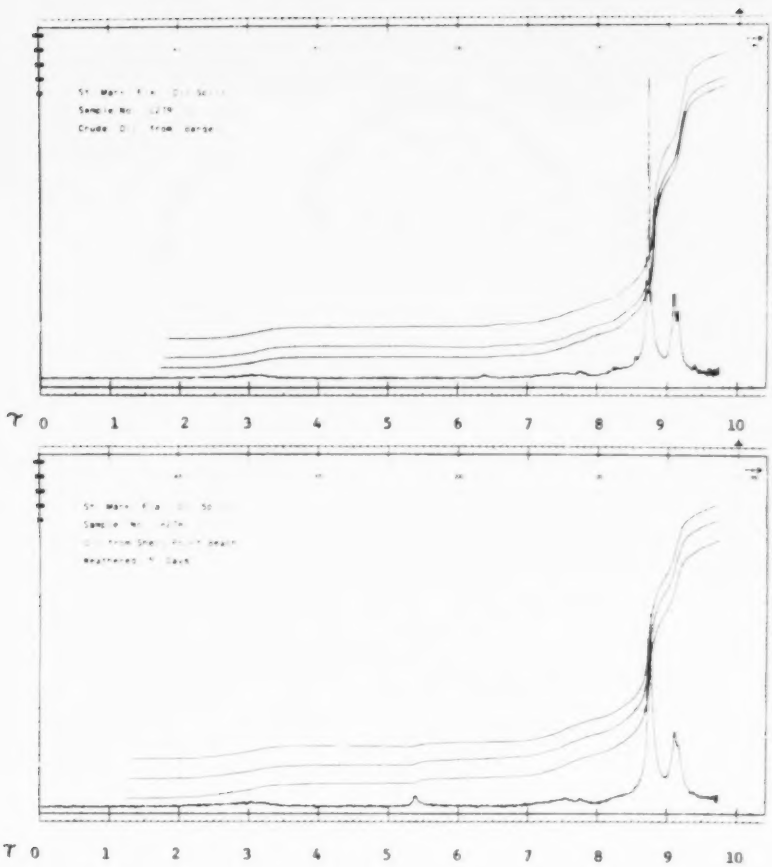


Figure 26. Comparison of NMR Spectra of Oil from the Suspect Barge and from a Florida Beach

Table 16

Normalized Peak Areas of Proton Signals in Samples from the St. Mark, Florida, Oil Spill

Sample	τ 9.05-9.60	τ 8.00-9.05	τ 6.80-3.00	τ 2.00-4.00
Crude oil from barge (Figure 26, top)	0.27	0.60	0.08	0.04
Sample from Shell Point Beach-- Weathered 3 days	0.23	0.62	0.09	0.06
Sample from Shell Point Beach Weeds-- Weathered 5 days (Figure 26, bottom)	0.23	0.62	0.11	0.05
Sample from Shell Point Beach Weeds-- Weathered 7 days	0.21	0.65	0.11	0.04

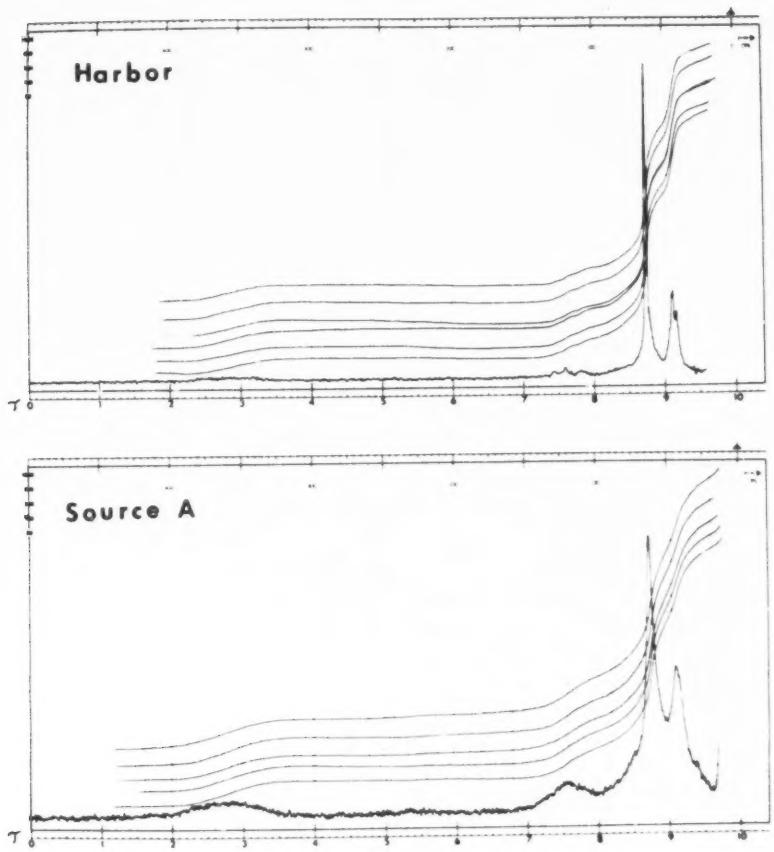


Figure 27. Comparison of NMR Spectra of Oil from Duluth Harbor and the Primary Suspect Source

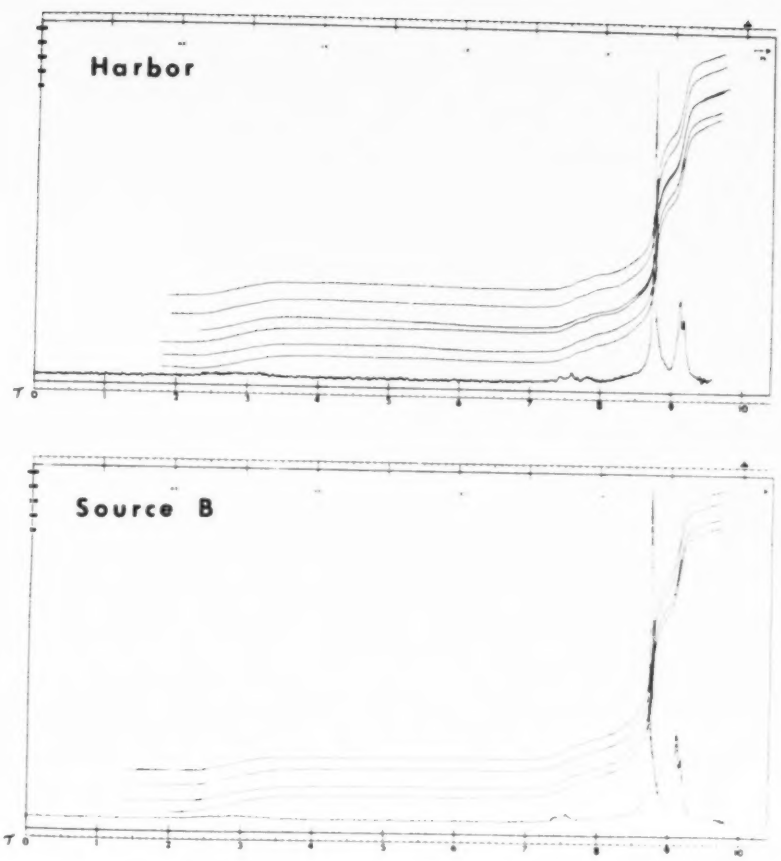


Figure 28. Comparison of NMR Spectra of Oil from Duluth Harbor and the Secondary Suspect Source

The similarity between the chemical shifts and the relative peak areas of each signal indicates that the samples are all of the same oil type and that the barge could have been the source of the spill. A comparison of infrared spectra and the sulfur and vanadium content of pollution samples with those of oil from the suspect barge also indicated that they were the same.

Small but distinct differences appeared between the barge sample and the spill samples and also among the spill samples themselves. The weathered samples showed a decrease in the relative CH_3 signal area and an increase in the CH_2 signal area as weathering time increased. A mixture of hydrocarbons containing both volatiles and nonvolatiles would be expected to show such relative change in signal areas. The volatile materials, having a larger ratio of CH_3 to CH_2 groups, evaporate faster, leaving the long chain hydrocarbons and other larger molecules behind. The result is a decrease in the CH_3 to CH_2 ratio.

Duluth Harbor Oil Pollution

In 1969, the harbormaster in Duluth, Minnesota, submitted samples of oil from the persistently polluted harbor to the National Water Quality Laboratory in Duluth. These samples and samples of a suspected source (a railway company) were sent to NWCCRP for NMR analyses. Also sent later was a sample from a second possible source, an oil company.

The NMR spectrum of the harbor sample was very different from that of the railway company sample (Figure 27). It closely resembled, however, the spectrum of the oil company sample (Figure 28) implicating the oil company as the probable source of pollution. Prosecution of the oil company resulted in conviction and a fine.

Tampa Bay Oil Spill

The *Alcoa Trader* was suspected to be the source of an oil slick on Tampa Bay, Florida, in 1969. However, NMR spectra of samples from the slick and from the ship's oil cargo displayed significant differences. The proportions of the various types of protons in the

samples as calculated from the integrated intensities are presented below:

	Methyl	Methylene	Misc.	Aromatic
Tampa Bay Sample	0.20	0.55	0.16	0.10
Alcoa Trader Sample	0.28	0.61	0.07	0.04

The differences in the spectra are not believed to be due merely to weathering effects on the slick samples since the changes in some proton proportions do not correspond to those predicted from weathering. In studies of the weathering on other oil samples (crude oil and Bunker C) three changes were noted:

- weathering lowers the proportion of methyl proton,
- it increases the methylene proton proportion, and
- it has a small or no effect on the aromatic proton percentage.

On the bases of these data, therefore, the oil from the slick was judged to be from a source other than the *Alcoa Trader* or was highly contaminated with oil from another source.

Florida West Coast Oil Contamination

In the spring of 1970, oil pollution was reported along an 80-100 mile stretch of Florida's northwest coast. Two possible sources were the Greek tanker, *Delian Apollon*, wrecked off Tampa in February, 1970, carrying Bunker C oil, and a large Chevron crude oil fire from a well off the coast of Louisiana. Because the two sources represented two different types of oil, the analysis was performed by NMR.

Spectra were scanned of samples from the two suspected sources and from the polluted areas (Pensacola Beach, Panama City Beach, St. Andrews Park, Indian Pass, Destin Beach, and submerged oil out from Destin Beach). Data are summarized in Table 17 along with data from previous weathering studies on Bunker C and crude oil.

Table 17

NMR Comparison of Oil from West Florida Beaches with Suspect Crude Oil and Bunker C Oil

Sample	Normalized Proton Signal Areas			
	Methyl	Methylene	Misc.	Aromatic
Environmental samples	0.21-0.22	0.68-0.71	0.05-0.07	0.02-0.04
Delian Appollon	0.22	0.61	0.10	0.07
Chevron oil well and oil slick	0.26-0.27	0.65-0.66	0.05	0.02-0.03
Weathered Bunker C	0.17-0.21	0.56-0.59	0.10-0.15	0.10-0.13
Weathered crude	0.21-0.24	0.69-0.71	0.04-0.06	0.02-0.03

The spectra of the spill samples were all similar and matched those of weathered crude oil but not those of Bunker C or weathered Bunker C oil.

The Chevron oil well crude oil was therefore indicated as the more probable source of the pollution.

Miscellaneous Oil Analyses

In the fall of 1970 an oil slick was discovered by the U. S. Coast Guard around the Dutch Cargo carrier *Maya*. Samples of the oil slick, of water being discharged from the *Maya* and of the oil in the bilge of the *Maya* were taken for analysis by EPA Region IV Surveillance and Analysis Division at SERL. An NMR analysis was also requested since prosecution was expected and confirmatory data were desired to show that the ship was the source of the slick.

The NMR spectra of the samples were all similar, indicating a partially refined crude oil. Infrared analysis likewise confirmed that the samples were all very similar and probably from the same source. The data were entered as evidence in court by the State of Florida. The case, however, has been postponed by a Federal injunction charging that Florida's coastal pollution laws are unconstitutional.

In the winter of 1970 Mr. Warren T. McFall, EPA Alaska operations Office, requested an analysis of oil on the feathers of a bird that had been killed by oil pollution and crude oil from a suspect source near Cook Inlet. The NMR spectra of the two samples were quite different--more than would be expected from weathering and contamination from the bird's natural oils. Fluorescence data also indicated that the two were not from the same source. We concluded that the Cook Inlet crude oil was not the source of the oil that killed the bird. No further work was done concerning this problem.

Also in the winter of 1970, the Chemical Services Branch received an oil sample taken by the National Marine Fisheries Service during exploratory fishing at 330 fathoms northwest of the Dutch West Indies island of Aruba. From NMR analysis we concluded that the oil was unlike any crude, Bunker C or refined oils that we examined previously. The source remains unknown.

11. Analysis of Oil Spills by Fluorescence Spectroscopy

Fluorescence spectroscopy represents yet another method of analysis that may be used to characterize an oil spill and determine its source. Whereas NMR can differentiate only between oil types, different oils of the same type have sufficiently distinctive fluorescence characteristics to distinguish between them (15).

Several samples are cited comparing fluorescence data from oil spills with data from other techniques.

Duluth Harbor Oil Pollution

In a Duluth Harbor oil spill mentioned previously the NMR spectra indicated that the oil of the slick matched that of the suspect oil company and did not match any of three oil samples from the suspect railway company. Fluorescence analysis showed that the railway samples were radically different from the harbor oil, corroborating NMR conclusions.

NMR spectra of both oil slick samples and the samples from the oil company, however, were identical. Also, the relative fluorescent intensities of the oil company samples and the intensity ratios closely matched those of the first of the two harbor samples (Table 13).

Harbor Sample #2 did not match the oil company samples as well. But a mixture of 1 part oil from the railway company and 14 parts oil from the oil company produced a fluorescence spectrum similar to that of the second harbor sample. Thus, although the oil company was the main source of the pollution there was evidence of a measurable contribution from the railway company.

Savannah River Spills

In April of 1971, two different oil spills occurred on the Savannah River. Fluorescence analyses were performed on the spill samples and on samples from suspect sources. The data obtained were compared with that from gas chromatographic analysis using flame ionization and photometric detectors.

Table 18

Fluorescence Spectra of Duluth Harbor Samples

Samples	Fluorescence Spectra (Excitation at 340 mμ)			
	Intensity ratio at 400 mμ of harbor sample/oil co.		Intensity ratio, shoulder at 440 mμ/max at 400 mμ	
	Dilution 1:1000	Dilution 1:10,000	Dilution 1:1000	Dilution 1:10,000
Harbor Sample #1	0.97	1.00	0.39	0.30
Harbor Sample #2	1.98	3.67	0.58	0.48
Oil Co. Sample #1	1.14	0.97	0.40	0.31
Oil Co. Sample #2	1.00	1.00	0.41	0.30
Oil Co. Sample #3	1.00	0.90	0.39	0.37

Table 19

Fluorescence Spectra of Savannah River Samples

Spill	Sample	10,000 Dilution		50,000 Dilution	
		Maximum intensity	440 nm / 368 nm	Maximum intensity	440 nm / 385 nm
Spill A	Fuel line	100	.40	100	.40
	Drip pan	17	.15	21	.22
	Bilge	72	.35	75	.32
	River sample #1*	92	.40	93	.40
	River sample #2*	95	.40	94	.39
Spill B	Suspect	100	.80	100	.66
	River sample	46	.55	42	.49

*The 440nm/368nm ratios of the spill and suspect match very well. The intensity readings are slightly low for the two spill samples but this is not uncommon for oils that have been weathered.

Spill "A"

Two samples from spill "A" were compared by fluorescence analysis with three oils taken from the fuel line, a drip pan, and the bilge of a nearby suspect ship.

Fluorescence data are presented in Table 19. The relative intensity measurements from the spill samples matched those of the fuel line from the ship, confirming results of GC analysis.

Spill "B"

In the second spill, which appeared to be a Bunker fuel, the suspected source was the fuel tank of a nearby vessel. The fluorescence data (Table 19), however, indicated that the two oils were not similar, again confirming GC data.

Duluth Superior Harbor Spill

In an oil spill on Duluth Superior Harbor in 1970 a British and an American ship were suspects. Spill samples were collected from the bay and from the slip in which both ships had been docked at different times. Comparisons were made with oils obtained from the ships. Each sample was diluted with oils obtained from the ships. Each sample was diluted wt/vol 1:7500, 1:10,000, and 1:100,000 with cyclohexane. The relative fluorescence intensity data for the spill and suspect samples are presented in Table 20.

All parameters of the sample from the British freighter match closely those of the spill sample, implicating that ship as the source of the pollution. These results were turned over the Coast Guard for legal action.

Dundee Canal, Savannah River

An oil spill covering a two to three mile length of the Dundee Canal occurred in February, 1971. A tank trailer carrying Bunker fuel was the suspect source. Five spill samples and a sample from the trailer were collected. The broad range of intensity values (Table 21) at 1:50,000 dilution indicates weathering of the spill

Table 20

Fluorescence Spectra of the Duluth Superior Harbor Samples

Sample	Intensity @ 386nm			Intensity ratio 440nm/386nm		
	Dilution 1:7,500	Dilution 1:10,000	Dilution 1:100,000	Dilution 1:7,500	Dilution 1:10,000	Dilution 1:100,000
British freighter	94	87	65	0.67	0.64	0.57
American freighter	30	20	6	0.24	0.25	0.28
Spill sample	93	81	52	0.63	0.60	0.55

Table 21

Fluorescence Spectra of the Dundee Canal Samples

Samples	1:10,000 Dilution		1:50,000 Dilution				
	Max. Intensity	Ratio $\frac{440\ nm}{386\ nm}$	Max. Intensity	Ratio $\frac{440\ nm}{386\ nm}$	Ni (ppm)	V (ppm)	Ni/V
Suspect tank trailer #82	100	.66	100	.56	44	365	.12
#1--Puddle on ground behind trailer	91	.60	69	.53	28	198	.14
#2--Ditch along Hwy 80 under highway	94	.64	73	.56	32	285	.11
#3--Ditch along Hwy 80	97	.65	84	.56	33	308	.11
#4--Dundee Canal	100	.66	94	.57	43	348	.12
#5--Dundee Canal at Savannah River	77	.59	54	.50	25	210	.12

samples. A decrease in fluorescence intensity is common in weathered oil.

Fluorescence data confirmed the metal ratio (Ni/V) analyses and GC data indicating that the spilled oil was non-homogeneous. Spill sample #4 (Dundee Canal), however, matched the suspect oil in all parameters.

St. Johns River, Jacksonville, Florida

An oil spill occurring in the St. Johns River covered a one square mile area. Four samples (numbered 1-4) were taken from the slick and six suspect samples (numbered 5-10) were collected from oil depots, ships, and industries surrounding the spill area. All samples were cleaned, dried, and analyzed by the Region IV Chemical Services Branch for four parameters: 1) percent sulphur, 2) nickel-vanadium ratios, 3) infrared ratios, and 4) color comparison under UV light. The NWCCRP was requested to analyze the samples by the fluorescence technique.

Fluorescence spectra were taken at various dilutions of the oils with cyclohexane (1:10,000, 1:50,000 and 1:100,000). The ratio of the maximum intensity (386 nm) to that of a shoulder (440 nm) was calculated for each spectrum (15). Table 22 summarizes the data for fluorescence analyses and Table 23 summarizes the results of the other analyses. Both sets of data indicate that the four spill samples came from the same source.

Of the six suspect samples, only one matched the spill sample in all fluorescence parameters. The same suspect sample matched the spill with all other analytical techniques employed, confirming the identification.

Table 22

Fluorescence Spectra of St. John's River Samples

Sample no.	Maximum intensity at 386 nm			Intensity ratio shoulder at 440 nm/386 nm max.			Parameters that agree
	Dilution 1:10,000	Dilution 1:50,000	Dilution 1:100,000	Dilution 1:10,000	Dilution 1:50,000	Dilution 1:100,000	
			Spill samples				
1	70	77	72	0.67	0.60	0.54	
2	65	81	90	0.70	0.61	0.55	
3	66	72	76	0.71	0.63	0.55	
4	72	72	75	0.67	0.61	0.53	
Range of spill samples	65-72	72-81	72-90	0.67-0.71	0.60-0.63	0.53-0.55	
			Suspect samples				
5	67	81	90	0.71	0.63	0.55	6 of 6
6	50	60	64	0.62	0.55	0.47	0 of 6
7	73	68	65	0.57	0.53	0.45	0 of 6
8	78	76	71	0.58	0.52	0.45	1 of 6
9	50[a]	73	99	0.82[a]	0.72	0.59	1 of 6
10	100	100	100	0.56	0.51	0.44	0 of 6

[a]Maximum is at 405 nm instead of 386 nm.

Table 23

Other Analyses of St. John's River Samples

Sample no.	% Sulfur	Ni/V	Infrared ratios: 720 cm^{-1} / 1375 cm^{-1}	3050 cm^{-1} / 2925 cm^{-1}	810 cm^{-1} / 1375 cm^{-1}	810 cm^{-1} / 720 cm^{-1}	1600 cm^{-1} / 1375 cm^{-1}	uv Colors	Parameters that agree
1	[a]	[a]	0.28	0.023	0.24	0.88	0.13	yellow	
2	2.59	0.31	0.29	0.020	0.27	0.94	0.15	yellow	
3	2.78	0.38	0.34	0.034	0.36	1.09	0.18	yellow	
4	2.62	0.29	0.31	0.026	0.26	0.86	0.16	yellow	
Range of spill	2.59-2.78	0.29-0.38	0.28-0.34	0.020-0.034	0.24-0.36	0.86-1.09	0.13-0.18	yellow	
5	2.65	0.31	0.29	0.023	0.27	0.95	0.16	same yellow	8 of 8
6	2.30	0.19	0.19	0.023	0.25	1.34	0.15	darker (brown)	3 of 8
7	2.56	0.27	0.33	0.023	0.20	0.60	0.09	lighter (yellow)	2 of 8
8	2.02	0.21	0.26	0.017	0.21	0.82	0.11	lighter (yellow)	0 of 8
9	2.08	0.61	0.35	0.041	0.47	1.36	0.27	darker (brown)	0 of 8
10	1.68	0.24	0.16	0.034	0.26	1.66	0.14	lighter (yellow)	

[a]Sample no. 1 did not contain enough oil for sulfur, nickel, or vanadium analysis.

SECTION V

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